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AN INVESTIGATION OF TECHNIQUES FOR REMOVAL OF CHROMIUM FROM ELECTRO-PLATING WASTES

G. R. Smithson, Jr.

Battelle Memorial Institute

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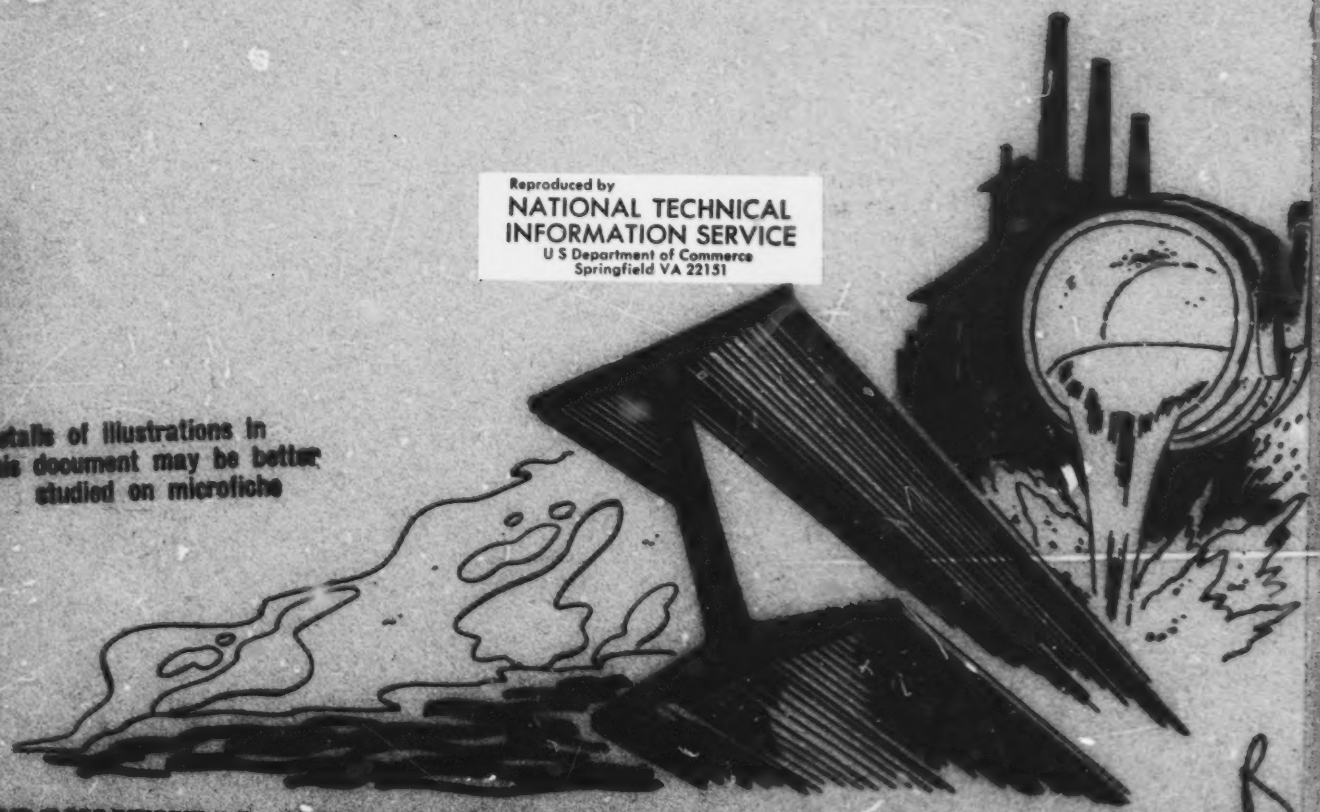

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The results of the various phases of the study indicated that activated carbon adsorption for chromium removal may have practical application in many small plating plants. Further development of the process was recommended in actual plating plant installations.

This report was submitted by Battelle Memorial Institute, Columbus Laboratories, in partial fulfillment of Grant Project 12010 EIE by the Industrial Pollution Control Branch, Environmental Protection Agency to the Metal Finisher's Foundation.

Abstractor Edward L. Dulaney — Water Quality Research, EPA

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AN INVESTIGATION OF TECHNIQUES FOR REMOVAL OF CHROMIUM FROM ELECTROPLATING WASTES

Sponsored by

INDUSTRIAL POLLUTION CONTROL BRANCH

ENVIRONMENTAL PROTECTION AGENCY

and

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Prepared by

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Columbus Laboratories

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ABSTRACT

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Key Words: Electroplating wastes

Chromium

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Activated carbon

CONTENTS

Section		Page
I	CONCLUSIONS	1
II	RECOMMENDATIONS	3
III	INTRODUCTION	5
IV	BACKGROUND INFORMATION	7
	State of the Art of Metal-Finishing Waste Treatment	7
	Current Practices in Small Electroplating Plants	7
	Production Characteristics	7
	Waste-Effluent Volumes and Compositions	9
V	EXPERIMENTAL WORK	13
	Phase 1: Preliminary Experimental Study	13
	General Scope of Investigation	13
	Ion Flotation Studies	13
	General Description of Method	13
	Equipment and Procedure	14
	Results	17
	Activated Carbon Adsorption Studies	25
	General Description of Method	25
	Equipment and Procedure	26
	Results	29
	Liquid-Liquid Extraction Studies	40
	General Description of Method	40
	Chemistry of Liquid-Liquid Extraction	42
	Requirements for Feasibility	43
	Equipment and Procedure	44

CONTENTS (Cont.)

Section		Page
	Results	46
	Regeneration	48
	Treatability of the Strip Solution	49
	Other Techniques Evaluated	51
	Reduction of Chromium with Activated Carbon	51
	Reverse Osmosis for Chromium Removal	51
	Adsorption of Chromium on Activated Alumina	52
	Preliminary Evaluation of Treatment Costs	52
	Ion Flotation	53
	Adsorption on Activated Carbon	54
	Liquid-Liquid Extraction	56
	Comparison of Experimental and Conventional Processes	59
	Phase 2: Demonstration Plant Study	60
	Pilot-Scale Investigation	62
	Equipment and Procedure	62
	Results of Sulfuric Acid Regeneration Method	64
	Results of Caustic Regeneration Method	67
	Discussion of Pilot-Plant Runs	67
VI	ECONOMIC EVALUATION OF PROCESS	77
VII	ACKNOWLEDGMENTS	81
VIII	BIBLIOGRAPHY	83
IX	APPENDICES	85
	Conventional Methods for Treatment of Chromium Wastewater.	87
	Methods used for Control Analyses	89

FIGURES

		Page
1	CALCULATED LEVELS OF CHROMIUM AND CYANIDE DISCHARGED BY NAMF MEMBER PLANTS	10
2	WATER USAGE BY NAMF MEMBER PLANTS	11
3	STANDARD LABORATORY FLOTATION CELL FOR THE ION FLOTATION EXPERIMENTS	15
4	SKETCH OF FLOTATION CELL	16
5	EFFICIENCY OF VARIOUS COLLECTORS FOR CHROMIUM REMOVAL FROM 100 PPM SOLUTION	21
6	EFFICIENCY OF VARIOUS COLLECTORS FOR CHROMIUM REMOVAL FROM 10 PPM SOLUTION	22
7	BENCH-SCALE CONTINUOUS COLUMNS FOR ADSORPTION EXPERIMENTS	28
8	AMOUNT OF POWDERED ACTIVATED CARBON REQUIRED FOR HEXAVALENT CHROMIUM REMOVAL	31
9	EFFECT OF CONTACT TIME ON CHROMIUM REMOVAL	32
10	EFFECT OF pH ON CHROMIUM REMOVAL	33
11	TYPICAL ADSORPTION ISOTHERMS FOR HEXAVALENT CHROMIUM	35
12	EXAMPLE OF TWO-STAGE EXTRACTION, SINGLE-STAGE STRIPPING LIQUID-LIQUID EXTRACTION PROCESS	41
13	BENCH-SCALE MORRIS-TYPE CONTACTOR FOR CONTINUOUS LIQUID-LIQUID EXTRACTION EXPERIMENTS	45
14	FLOWSHEET ASSUMED FOR COST ESTIMATES	57
15	ALTERNATIVE PROCESSES FOR CHROMIUM REMOVAL BY ACTIVATED CARBON	61
16	PILOT-PLANT CARBON ADSORPTION SYSTEM	63
17	PILOT-PLANT DATA ON ADSORPTION AND ACID REGENERATION	68
18	PILOT-PLANT DATA ON ADSORPTION AND CAUSTIC REGENERATION	71
19	ADSORPTION CAPACITIES FOR HEXAVALENT CHROMIUM AFTER MULTIPLE CYCLES WITH INTERMEDIATE CAUSTIC REGENERATION	73
20	ADSORPTION CAPACITIES FOR HEXAVALENT CHROMIUM AFTER MULTIPLE CYCLES WITH INTERMEDIATE ACID REGENERATION	74
21	EFFECT OF OPERATING CYCLES ON CHEMICAL COSTS FOR TWO REGENERATION METHODS	79
22	STANDARD CHROMIUM CURVE	91

TABLES

No.		Page
1	SUMMARY OF NAMF MEMBER PLANTS IN WHICH CHROMIUM AND/OR CYANIDES ARE USED	8
2	SUMMARY OF RINSING PRACTICES IN NAMF MEMBER PLANTS	8
3	SUMMARY OF DISPOSAL METHODS USED BY NAMF MEMBER PLANTS	8
4	CONCENTRATIONS OF CHROMIUM AND CYANIDE IN VARIOUS WASTE STREAMS FROM NAMF MEMBER PLANTS	12
5	TYPICAL CONCENTRATION OF HEAVY METALS IN COMBINED EFFLUENTS FROM SEVERAL NAMF MEMBER PLANTS	12
6	TECHNIQUES EVALUATED EXPERIMENTALLY	13
7	EXPERIMENTAL DATA ON VARIOUS COLLECTORS FOR FLOTATION OF HEXAVALENT CHROMIUM	18
8	FLOTATION DATA SHOWING THE EFFECT OF pH ON REMOVAL OF HEXAVALENT CHROMIUM	19
9	FLOTATION DATA ON CHROMIUM-CONTAINING SOLUTIONS AT VARIOUS INITIAL CONCENTRATIONS	20
10	EXPERIMENTAL DATA ON THE REGENERATION AND REUSE OF FLOTATION COLLECTOR FOR HEXAVALENT CHROMIUM	24
11	FLOTATION DATA ON SOLUTIONS CONTAINING TRIVALENT CHROMIUM	25
12	TYPES OF ACTIVATED CARBON EVALUATED	27
13	REMOVAL OF HEXAVALENT CHROMIUM WITH VARIOUS TYPES OF ACTIVATED CARBON	30
14	COMPARISON OF GRANULAR AND PULVERIZED ACTIVATED CARBON FOR CHROMIUM REMOVAL AT VARIOUS CONCENTRATIONS	36
15	CONTINUOUS EXPERIMENTS ON ADSORPTION OF CHROMIUM WITH ACTIVATED CARBON	37
16	REGENERATION OF CARBON FROM CHROMIUM ADSORPTION EXPERIMENTS	39
17	PERFORMANCE OF SEVERAL AMINES IN THE BATCH EXTRACTION OF HEXAVALENT CHROMIUM	47
18	BATCH EXTRACTION OF HEXAVALENT CHROMIUM FROM MORE CONCENTRATED SOLUTIONS USING ALAMINE 336	46
19	EXTRACTION OF HEXAVALENT CHROMIUM IN CONTINUOUS OPERATIONS	48
20	EXPERIMENTAL DATA ON CHROMIUM REMOVAL BY REVERSE OSMOSIS	51
21	EFFICIENCY AND COSTS OF ION FLOTATION COLLECTORS FOR CHROMIUM REMOVAL	53
22	ESTIMATED REAGENT COSTS FOR ACTIVATED CARBON REGENERATION AFTER ADSORPTION OF CHROMIUM	55

TABLES (Cont.)

No.		Page
23	ECONOMIC FACTORS IN OPERATING COSTS FOR LIQUID-LIQUID EXTRACTION	58
24	PRELIMINARY COMPARISON OF COSTS FOR SELECTED EXPERIMENTAL AND CONVENTIONAL TREATMENT METHODS	59
25	PILOT-PLANT ADSORPTION DATA ON COLUMN NO. 1, ACID REGENERATION	65
26	PILOT-PLANT REGENERATION DATA ON COLUMN NO. 1	66
27	PILOT-PLANT ADSORPTION DATA ON COLUMN NO. 2, CAUSTIC REGENERATION	69
28	PILOT-PLANT REGENERATION DATA ON COLUMN NO. 2	70
29	COMPARISON OF CHEMICAL COSTS FOR ACTIVATED CARBON ADSORPTION AND CONVENTIONAL TREATMENT	78
30	ESSENTIAL PLANT AND OPERATING COSTS FOR CARBON ADSORPTION AND CONVENTIONAL TREATMENT PROCESSES	80

SECTION I

CONCLUSIONS

(1) The use of waste treatment systems by small electroplating plants is not yet required in many locations. Adequate technology, however, is available for treating these wastes to any required degree of detoxification by conventional processes prior to discharge into sewers or other receiving waters.

(2) On the basis of laboratory studies, several nonconventional processes are technically feasible for the treatment of chromium rinse waters. These are: activated-carbon adsorption, ion flotation, and solvent extraction.

(3) From a practical standpoint, an activated-carbon process has promise of excelling the conventional methods for treatment of chromium rinse waters from small plating shops. The carbon process may have significant advantages in low capital investment, simple and continuous operation, and minimum floor space requirements, all of which are particularly important to the small plater.

(4) The carbon process has been shown feasible on a pilot-plant scale with actual chromium rinse waters from a small plating company. The system can be operated with removal efficiencies greater than 99 percent for hexavalent chromium. Removal of total chromium is about 95 percent. The process also provides for partial recovery of the removed chromium by caustic regeneration techniques or, alternately, the loaded carbon can be disposed of conveniently as a solid waste material. The carbon-adsorption process, as presently developed, is not optimum and very probably can be improved with additional study. The regeneration step, while workable, was not as efficient as originally anticipated. Improved regeneration, as might be realizable with continued operation, would enhance significantly the practical and economic feasibility of this process.

(5) Operating costs for a carbon process employing caustic regeneration are about $5.00 per 8-hour day on the basis of a 15-gpm waste stream containing 100 ppm of hexavalent chromium. This compares to an operating cost of about $7.00 for the conventional treatment method employing sodium bisulfite.

SECTION II

RECOMMENDATIONS

This program has involved an evaluation of both conventional and nonconventional processes for treating chromium rinse waters considering the technical and economic criteria believed applicable to small electroplating plants. The scope of the program was to develop processes for demonstration phase utilization. Based on the results obtained in the study, it was recommended that field testing of an activated-carbon process on chromium rinse waters be carried out.

For accurate definition of the full potential of the carbon adsorption process, the data obtained in this study should be extended. The pilot-plant runs, while demonstrating that carbon adsorption has the promise of becoming a very simple and economic process especially suitable for the smaller plater, have not provided a complete answer to several important questions:

(1) How can stripping be made more effective and complete?

(2) With better stripping, how much greater adsorptive capacity can be obtained per cycle and what effect will this have on the longevity of the carbon?

(3) What will be the precise effect of operation with waste solutions more dilute and more concentrated than the waste streams used in this study?

(4) To what extent will improved stripping and higher adsorption capacities enhance the practical and economic feasibility of the process?

(5) What is the impact of other metals, such as copper and nickel which were present to some extent in pilot-scale runs on the adsorption and stripping of chromium?

It is recommended that these factors be established firmly, not by any extension of a formal research program, but by installing units similar to the one used in this study in several plants and to have them operated over a period of at least 1 year.

Such continuing effort would be aimed at establishing design criteria in terms of the economic optimization of the carbon process in a variety of possible installations. These installations are recommended where (1) the waste flow is small and contains low concentrations of hexavalent chromium, (2) low-to-moderate quantities of waste chromium are involved, and a simple and convenient method of disposal is required, and (3) moderate quantities of chromium wastes are produced and the possibility exists for recovery of sodium chromate.

Very probably, some guidance and back-up laboratory work would be required. It is believed that much if not all of this could be done at the plant site by the selected companies themselves.

Battelle suggests that a plan for these extended runs be discussed in detail with officials of the Metal Finishers' Foundation.

SECTION III

INTRODUCTION

Many industries in the heavily industrialized areas of the United States are substantial contributors to the growing problem of water pollution. In many cases the wastes generated by industrial sources are carbonaceous and can be treated by biological methods or by incineration techniques. In other cases, however, the wastes are largely inorganic materials which cannot be disposed of by conventional techniques. Some of the most troublesome wastes are those generated in the production of inorganic chemicals and in various facets of the metallurgical industry. In the latter category, considerable attention has been directed toward abatement of pollution from waste pickle liquor from the steel industry and from metal-finishing wastes.

Electroplating and metal-finishing waste streams can contribute to stream pollution, either directly, owing to their content of toxic and corrosive materials, such as cyanide, acids, and metals; or indirectly, owing to the deleterious effect these components exert on biological sewage treatment systems. Federal, state, and municipal regulations fixing the allowable concentrations of the harmful components of these wastes already have been established. The restrictions are fairly rigorous at present. There is indication that they will, in many places, be made more rigorous in the future. Enforcement of regulations may be expected to become increasingly strict.

There is ample technology available for treating chromium and cyanide wastewaters to any required degree of detoxification. The conventional treatment methods, however, have been developed primarily for large electroplating plants where the relatively high cost of treatment can be absorbed. Economical methods have not been developed for the treatment of wastes from the relatively small electroplating shops. Currently many of these plants discharge their wastes into the city sewers and depend upon the municipal sewage plant for the removal of toxic materials.

More restrictive sewer ordinance and receiving water standards are major factors that make the development of economical techniques for treating the effluents from small electroplating facilities highly desirable. Another factor is the potential recovery of valuable metals from these waste streams.

The Pollution Abatement Committee of the Metal Finishers' Foundation, being acutely aware of this problem, authorized Battelle to undertake a study of existing hydrometallurgical techniques to determine their applicability to the treatment of wastes from smaller electroplating plants. This study, as proposed to the Metal Finishers' Foundation, was comprised of two phases:

Phase 1. Preliminary Experimental Study.
Phase 2. Demonstration Plant Study.

In each of these phases, chromium wastes and cyanide wastes were given separate study. This report presents the results, conclusions, and recommendations of the study on chromium wastes. A similar report will be prepared at a later date when the work on cyanide waste has been completed.

The first phase of the work on chromium was, in effect, a screening study, the overall objective of which was to pinpoint the processes best adapted technically and economically to the treatment of chromium wastes typical of those generated by the smaller plater. In this phase of the study, a thorough review of the present state of the art in the treatment of chromium waste was conducted; wastes from a selected sample of smaller plating establishments were characterized for volume and composition; and the various nonconventional approaches available to the smaller plater for treating his wastes were evaluated experimentally. As a result of this preliminary phase study, it was concluded that an activated carbon adsorption technique, a somewhat novel approach, gave promise of excelling the conventional process as a practical and economic method for treating chromium wastes from the typical smaller shop.

In the second phase of the work on chromium wastes, this carbon adsorption process was investigated on a pilot-plant scale. The pilot plant was set up in an actual plating plant (a member of the National Association of Metal Finishers) and operated over a 5-month period on this plants' normal reject rinse waters.

This study on chromium and cyanide emphasized only these two contaminants as contributing to the overall waste treatment problem. This, of course, overlooks other important contaminants, particularly heavy metals, which would be carried over in the combined wastewater stream. The development of an overall waste treatment approach which would remove these contaminants was beyond the scope of the current program.

SECTION IV

BACKGROUND INFORMATION

State of the Art of Metal-Finishing Waste Treatment

One of the initial efforts in this program was devoted to a survey of the open literature pertaining to waste treatment in the metal-finishing industry. This state-of-the-art survey emphasized such aspects as the nature of electroplating and metal-finishing wastes, current restrictions on their disposal, and conventional methods available for treatment of these wastes. The survey is presented in detail as a separate progress report on this program, designated 12010 EIE, dated November 15, 1968. It is not included within this report. However, for the purpose of comparing waste-treatment processes, a description of the conventional methods determined by this survey is included in the appendix. The review of these methods is intended to provide facts for the guidance of the smaller plater in the selection of a waste-treatment process. It should be pointed out, however, that these methods were developed more or less for use in larger electroplating plants having large volumes of wastewater. The use of these methods for treating low volumes of wastewater would certainly be feasible technically, but could be impractical or uneconomical for the smaller plater.

Current Practices in Small Electroplating Plants

Production Characteristics

One of the major efforts during the initial phase of the program was the accumulation of considerable data on the operating characteristics of small electroplating plants. These data were obtained by surveying member plants in NAMF via questionnaires. The survey emphasized primarily the extent of chromium- or cyanide-plating operations and certain aspects of these operations such as rinsing methods, disposal methods, chemical and water usage, etc. Questionnaires were sent to 655 U.S. members (foreign members were not included). In addition, 50 firms were asked to submit samples of combined and segregated rinse waters from their plant. Although only about 200 questionnaires were returned, a large number of firms were not involved in chromium or cyanide plating.

The basic production characteristics of NAMF member plants based on this survey are summarized in Tables 1, 2, and 3. Table 1 shows the number of plants which have chromium and/or cyanide plating operations. These data indicate that a large majority of the plants (81 percent) do both chromium and cyanide plating.

Table 2 shows the number of plants which currently have separate or combined rinsing circuits and whether or not it would be practical to separate these wastes. Table 3 indicates the current distribution of plants that employ sanitary sewers, lagoons, natural water bodies, etc., for

disposal of wastewaters. These data indicate that most of the plants use sanitary or storm sewers for disposal.

TABLE 1. SUMMARY OF NAMF MEMBER PLANTS IN WHICH CHROMIUM AND/OR CYANIDES ARE USED

	Number of Plants	Percent of Total
Plants with chromium only	24	13
Plants with cyanide only	11	6
Plants with both chromium and cyanides	151	81
Total	186	100

TABLE 2. SUMMARY OF RINSING PRACTICES IN NAMF MEMBER PLANTS

	Number of Plants	Percent of Total
Separate chromium and cyanide rinse circuits	84	47
Combined chromium and cyanide rinse circuits	94	53
Practical to separate wastes	71	42
Impractical to separate wastes	100	58

TABLE 3. SUMMARY OF DISPOSAL METHODS USED BY NAMF MEMBER PLANTS

	Number of Plants	Percent of Total
Municipal sanitary sewer	143	75
Storm sewer	24	12
Land disposal	5	3
Lagooning	3	2
Natural stream, lake, etc.	10	5
Others	6	3
Total	191	100

It is reasonable to presume that the response to the questionnaires constitutes a valid sample and that the information obtained is applicable to the association as a whole and possibly to the entire smaller shop plating industry.

Waste-Effluent Volumes and Compositions

The level of contaminants in wastewater from electroplating operations and the total volume of these wastes are also important factors in the evaluation of waste-treatment processes for small plating plants. Since this information is almost unavailable in the literature, the waste survey was used to provide data on these factors. NAMF member companies were asked to report their annual consumption of plating chemicals containing chromium and cyanide and the total annual water usage within the plant. For the purpose of estimating the amount of these plating chemicals which eventually appear in the wastewater, a loss factor of 80 percent was selected for both the chromium and cyanides.*

Based on this assumption, calculations were made of the total chromium, cyanide, and water discharged by each particular plant. A summarization of these data for all plants surveyed is shown in Figures 1 and 2. These graphs are important in establishing the approximate position of a particular plant within the industry and can be used to provide the following generalizations with regard to waste treatment methods. They are of importance in the assessment of:

(1) The general levels of chromium and cyanides likely to be discharged in the plant's wastewater

(2) The approximate annual cost for destruction of these contaminants within various segments of the industry

(3) Areas where recovery of plating chemicals and water should be considered.

In addition to the data shown in Figures 1 and 2, considerable data also were obtained on the actual composition of rinse waters generated by NAMF member plants. Selected plants submitted samples of their waste streams and these samples were analyzed to determine concentrations of cyanide, chromium, and other metals. Analytical data on chromium and cyanide levels in various waste streams are summarized in Table 4. Typical analyses for heavy metals in effluents from various plants are shown in Table 5. The data on chromium and cyanide indicate that cyanide concentrations are two to three times higher than chromium concentrations for combined effluents, which supports those data shown previously in Figure 1. Generally, it can be stated that concentrations will range from 10 to 100 ppm for either chromium or cyanide. Heavy metal concentrations, by contrast, generally fall below 10 ppm with the possible

*U.S. Bureau of Mines Information Circular 8058.

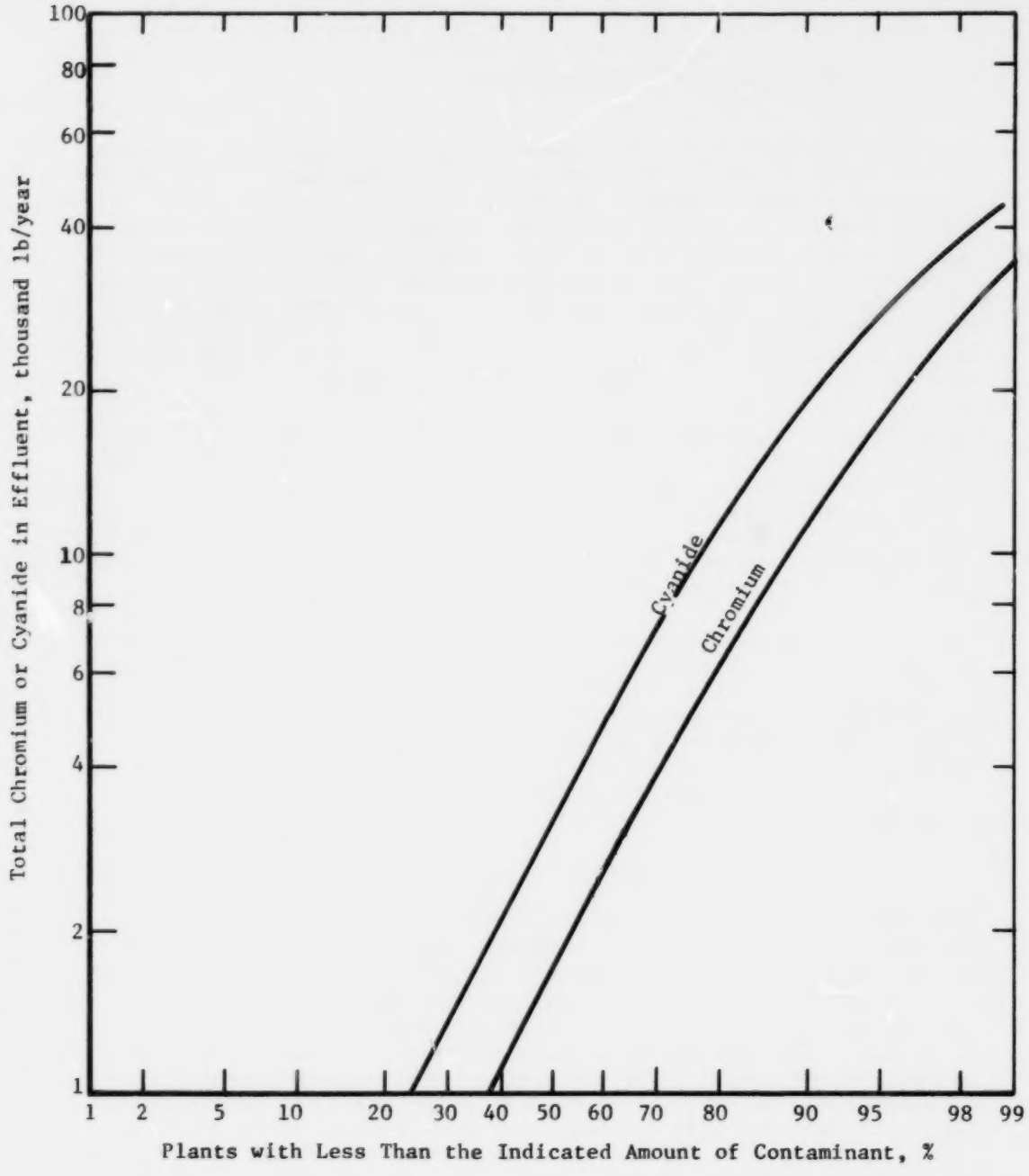


FIGURE 1. CALCULATED LEVELS OF CHROMIUM AND CYANIDE DISCHARGED BY NAMF MEMBER PLANTS

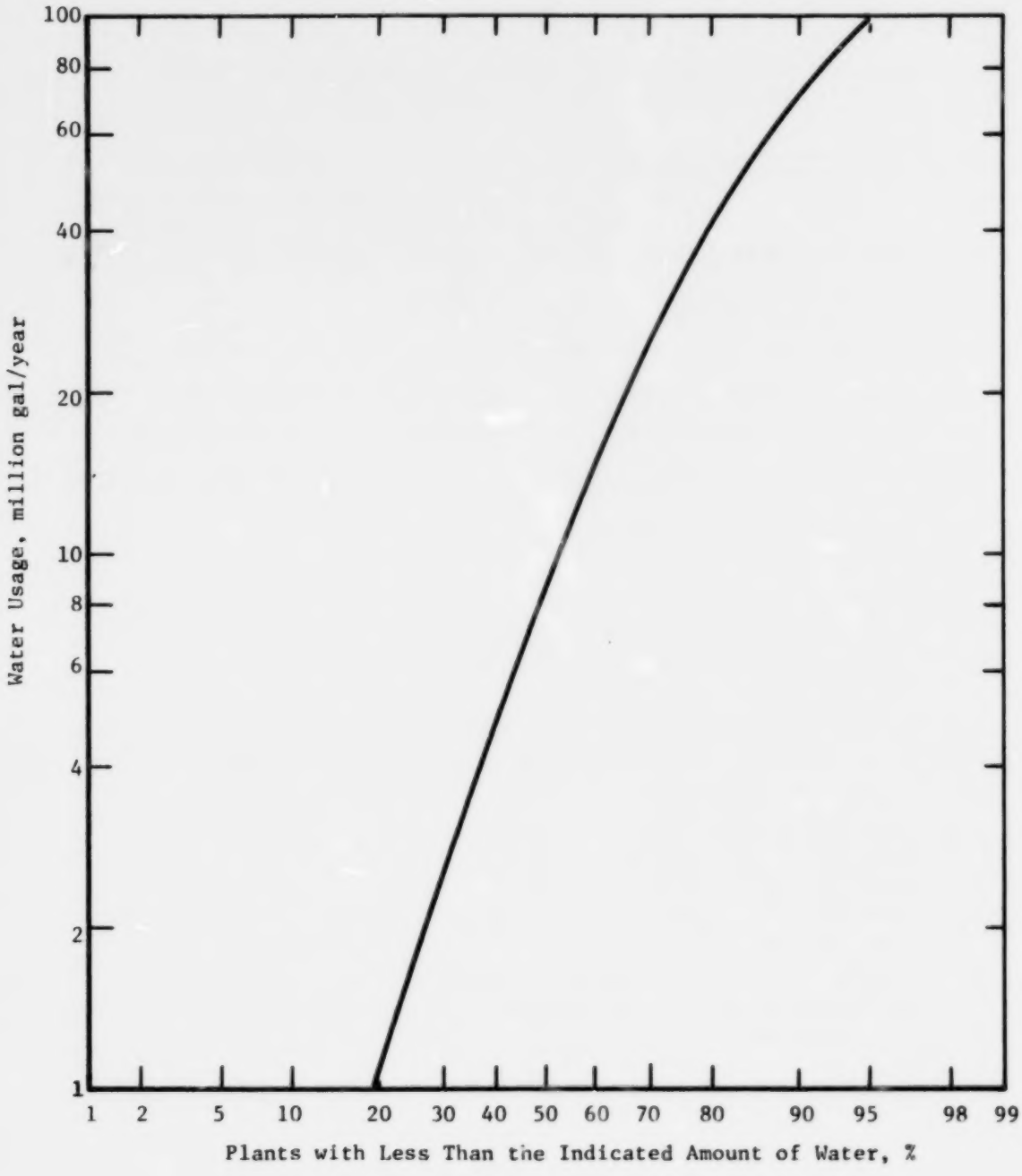


FIGURE 2. WATER USAGE BY NAMF MEMBER PLANTS

exceptions of copper and nickel. These elements were the major heavy metals found besides chromium in the particular samples which were analyzed.

TABLE 4. CONCENTRATIONS OF CHROMIUM AND CYANIDE IN VARIOUS WASTE STREAMS FROM NAMF MEMBER PLANTS[a]

Type of Sample	Number of Samples	Total Chromium, ppm[b]		Total Cyanide, ppm[c]	
		Range	Average	Range	Average
Separate chromium stream	9	15-70	41	--	--
Separate cyanide stream	7	--	--	9-115	72
Combined effluent	28	0-49	11	1-103	28

(a) Based on actual analyses by atomic adsorption and standard chemical techniques.
(b) Includes chromium contained in both the liquid and solid fractions of the sample.
(c) Cyanides in the liquid fraction, only.

TABLE 5. TYPICAL CONCENTRATION OF HEAVY METALS IN COMBINED EFFLUENTS FROM SEVERAL NAMF MEMBER PLANTS

	Concentration of Indicated Component, ppm[a]				
	Cu	Zn	Cd	Fe	Ni
Plant No. 4	31.0	5.0	<0.5	2.0	9.0
Plant No. 7	2.0	10.0	1.0	2.0	5.0
Plant No. 12	10.0	3.0	4.0	<2.0	58.0
Plant No. 15	36.0	<0.5	1.0	4.0	24.0
Plant No. 21	7.0	0.2	<0.5	2.0	23.0

(a) Based on analyses of samples by atomic adsorption techniques.

SECTION V

EXPERIMENTAL WORK

Phase 1: Preliminary Experimental Study

General Scope of Investigation

The initial phase of experimental work was limited to the investigation of "nonconventional" methods that might be applicable to the treatment of chromium rinse waters--the conventional methods of treatment having been thoroughly studied by numerous investigators for many years. At the outset of the program, the two most promising of the "nonconventional" approaches appeared to be:

(1) Ion flotation
(2) Liquid-liquid extraction.

These two approaches and a third--activated carbon adsorption--received major attention in the experimental program. During the course of the study, however, other approaches that would meet the qualifications of "nonconventional" and "suitable for rinse waters" suggested themselves and these were examined briefly. The "nonconventional" processes dealt with experimentally are listed in Table 6 and are described in the following sections of the report.

TABLE 6. TECHNIQUES EVALUATED EXPERIMENTALLY

	Applicability	
	Hexavalent Chromium	Trivalent Chromium
Ion Flotation	x	x
Activated Carbon Adsorption	x	
Liquid-Liquid Extraction	x	
Reduction by Activated Carbon	x	
Reverse Osmosis	x	
Adsorption on Activated Alumina	x	

Ion Flotation Studies

General Description of Method. Of the various techniques studied during this program, ion flotation probably is the most recently developed process. The technique of separating ions from aqueous solutions by

flotation has been recognized only for about 20 years. During this time, however, it has received significant development effort and is now becoming known as one of the basic chemical engineering unit processes.

Ion flotation is basically a combination of conventional mineral-flotation and ion-exchange processes. In mineral flotation, for example, finely divided solid particles are separated from a bulk solution by attachment to small air bubbles introduced into the liquid. The bubbles rise to the liquid surface, collapse, and form a froth which contains the solid material in concentrated form. An identical procedure is used in ion flotation to separate and concentrate ions from solution rather than solid particles.

The mechanism of bubble attachment in both flotation techniques is accomplished through the addition of a suitable collector. These collectors usually are some type of organic chemical having surface-active properties and are selective for only certain compounds. In addition to surface activity, the collectors for ion flotation have an inorganic group which ionizes in aqueous solutions and tends to make the collector partially soluble. The exchange of ions between the collector and solution is the basis for separation of certain ions from the solution.

Because ion flotation is especially effective for removing ions from extremely dilute solutions, it was given major attention during the experimental program. Its simplicity and low equipment costs enhanced its attractiveness for meeting the needs of the smaller plater.

Equipment and Procedure. The experimental apparatus for the study of the ion-flotation technique comprised both a specially designed glass flotation cell and a standard Denver laboratory cell which is designed for conventional flotation work. A photograph of the Denver cell is shown in Figure 3. Figure 4 is a sketch of the special glass cell.

The glass cell shown in Figure 4 was fabricated from a standard 500-cc graduated cylinder by installing ports for injecting flotation collector via a syringe and for withdrawing samples of the bulk solution. The cell contained an air-dispersion tube which was made of fritted glass with a porosity of 25 to 50 microns. During flotation, the air was generally admitted at a constant rate and was measured by a rotameter. The cell also was provided with an overflow tube which could be used to collect any foam produced during an experiment.

Generally, experiments in the small cell were conducted with a 300-cc volume of solution to be floated. The procedure used in conducting the majority of experiments was as follows:

(1) The cell was filled with 300 cc of the particular solution under study.

(2) The required flow of air was started (in most cases, a rate of 450 cc/minute was used).

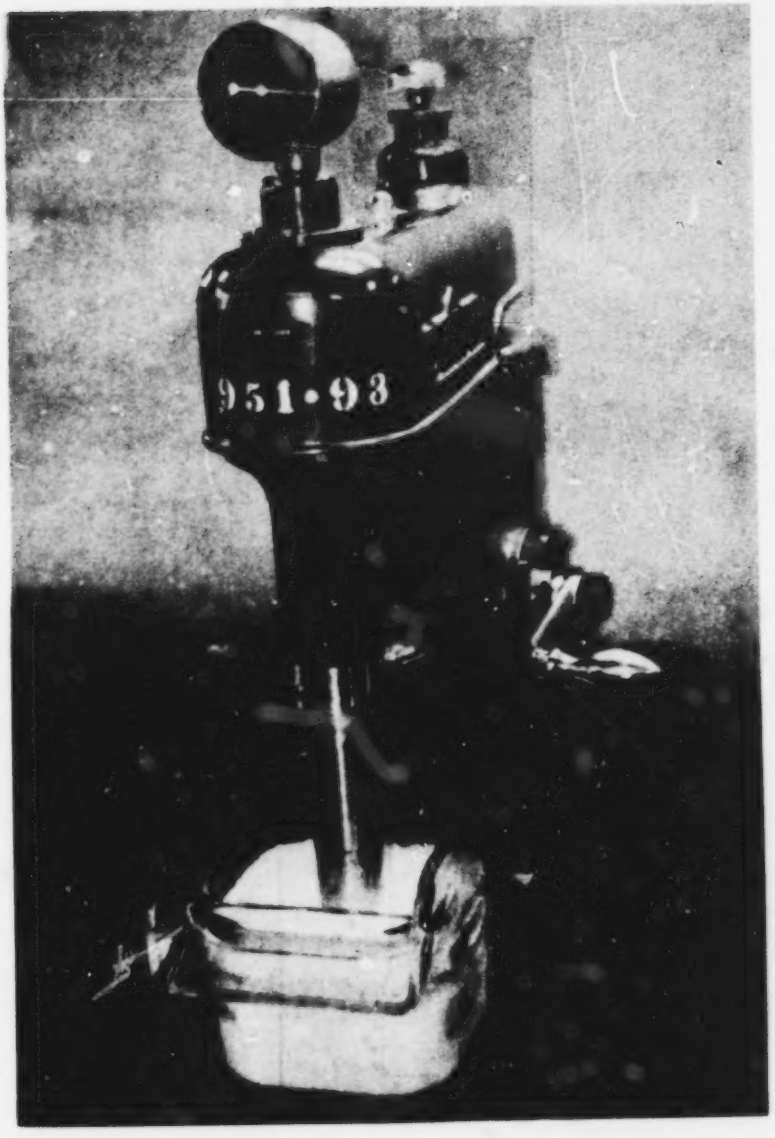


FIGURE 3. STANDARD LABORATORY FLOTATION CELL FOR THE ION FLOTATION EXPERIMENTS

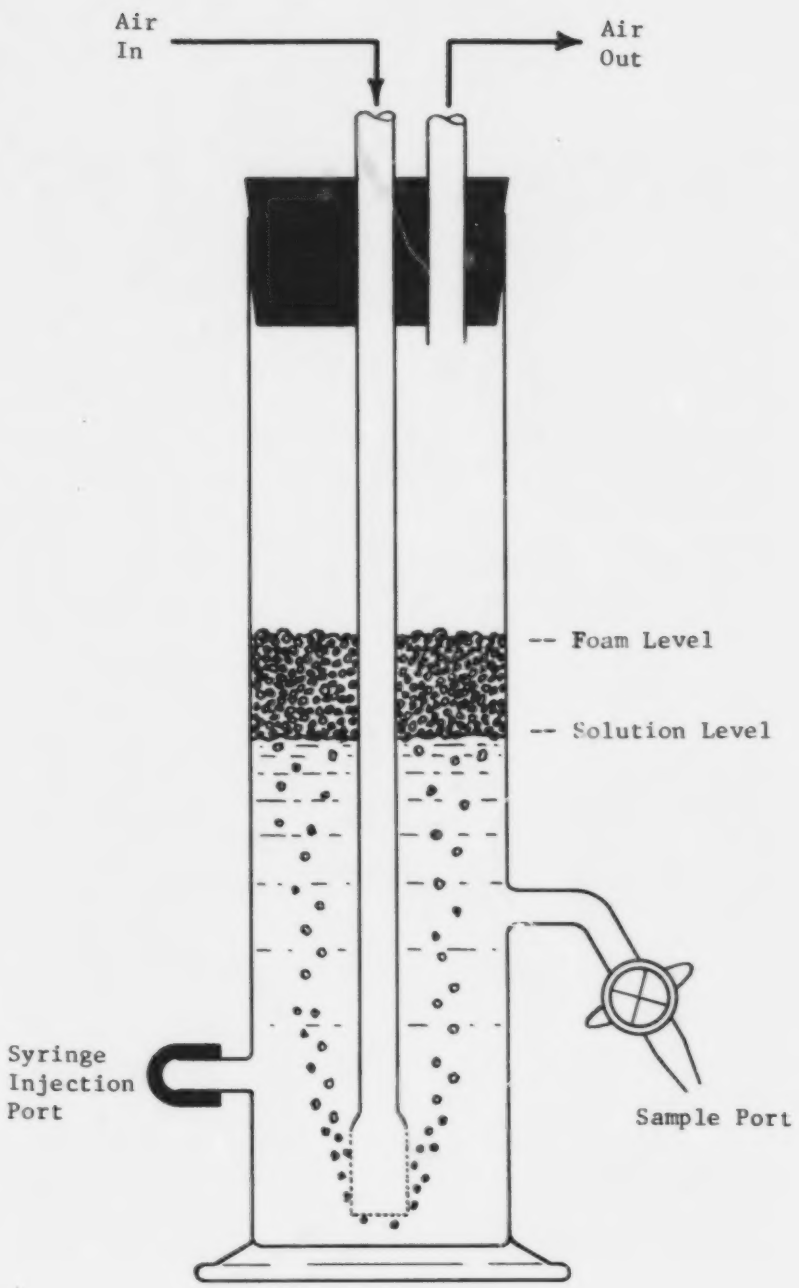


FIGURE 4. SKETCH OF FLOTATION CELL

(3) A preselected volume of collector solution was injected via the syringe port.

(4) After sufficient time had elapsed (generally 10 to 20 minutes), samples of the treated solution were obtained and saved for chemical analyses.

(5) Steps (3) and (4) were repeated until no further change occurred or until a specified total quantity of collector had been added.

(6) Samples were analyzed and the percentage extraction calculated.

The same general procedure was used for those experiments in the Denver laboratory cell except that the solution volume was usually 1 liter. Also, in several experiments involving regeneration or recovery, attempts were made to collect the entire flotation product which concentrated in the foam layer, whereas in the small glass cell this material was simply discarded after the run.

Results. Chromium Removal (Hexavalent). The initial experiments on ion flotation were conducted with the objective of screening several possible collectors which might be effective for removal of hexavalent chromium. The dichromate ion, being negatively charged, requires the addition of an anionic collector in order to effect flotation. Previous investigators have shown that certain anionic collectors, such as the long-chain quaternary-ammonium compounds, were effective for flotation of hexavalent chromium from aqueous solutions.

For the purpose of selecting a suitable collector, a total of seven anionic collectors were evaluated during this preliminary experimentation. The compounds selected for study consisted of primary, tertiary, or quaternary-ammonium compounds containing a long chain organic group of between 10 and 16 carbon atoms. Experiments were conducted with 10-ppm hexavalent chromium solution in the small glass flotation cell shown in Figure 4.

The particular collectors evaluated and the results of preliminary chromium-removal experiments are shown in Table 7. As shown by these data, significant extractions of chromium were achieved with several different collectors. The basic difference observed was that the primary amines [Collectors (1), (2), and (3) in Table 7] tended to form precipitates with dichromate ions and the operation could be classified essentially as precipitate flotation. Removal of chromium with the primary amines varied from 89 to 94 percent. The remaining collectors evaluated either did not significantly remove chromium or caused excessive foam formation and subsequent loss of solution from the cell. Collector (6), for example, which has been used in previous studies, removed about 70 percent of the chromium; however, the foam fraction amounted to more than half of the initial solution volume. This foaming tendency no doubt would produce a large volume of collapsed-foam solution in a continuously operated system and prevent the attainment of a high concentration of

TABLE 7. EXPERIMENTAL DATA ON VARIOUS COLLECTORS FOR FLOTATION OF HEXAVALENT CHROMIUM

Collector Used	Amount Used, cc(a)	pH	Chromium Concentration, ppm Initial	Chromium Concentration, ppm Final	Indicated Percent Removal
(1) Dodecylamine HCl	4.0	6.3	10.0	0.8	92
(2) Tetradecylamine HCl	3.0	6.3	10.0	0.6	94
(3) Hexadecylamine HCl	3.0	6.3	10.0	1.1	89
(4) N,N-Dimethyldodecylamine HCl	4.0	6.3	10.0	6.5	35
(5) Decyltrimethylammonium bromide	4.0	6.3	10.0	8.5	15
(6) Ethylhexadecyldimethylammonium bromide	0.5	6.3	10.0	3.2(b)	68
(7) Hexadecylpyridinium chloride	0.5	6.3	10.0	6.6(b)	34

(a) Solutions were made by dissolving chemical in isopropanol and adjusting to 20 gpl. The amine collectors also were neutralized with HCl to a pH of 7.

(b) Excessive foaming occurred during these runs causing loss of some solution.

chromium for final disposal. Collectors (4) through (7), although exhibiting true ion-flotation properties, were therefore eliminated from further consideration.

Subsequent experiments on hexavalent chromium solutions were conducted to investigate the effects of flotation variables on chromium extraction with a primary amine as collector. Among the variables believed to have significant effects on the process were solution pH, chromium concentration, and quantity of collector added.

Variations in solution pH were made within the limits of 2.0 and 10.0 using 10-ppm chromium solution with a C_{14} amine (tetradecylamine) as collector. The results of these experiments are summarized in Table 8. These data show that a wide range of pH could be used and still achieve effective removal of hexavalent chromium. Extractions greater than 90 percent were obtained within a pH range of 4.0 and 10.0. Below a pH of 4.0, however, the efficiency of removal decreased significantly. There was also an increased tendency for foaming at the lower pH values.

TABLE 8. FLOTATION DATA SHOWING THE EFFECT OF pH ON REMOVAL OF HEXAVALENT CHROMIUM

Initial pH	Amount of Collector Added[(a)], cc	Chromium Concentration, ppm		Indicated Percent Removal
		Initial	Final	
2.0	2	10	2.90	71.0
3.0	2	10	1.75	82.5
4.0	2	10	0.85	91.5
4.0	3	10	0.67	93.3
6.0	3	10	0.60	94.0
8.0	3	10	0.27	97.3
10.0	3	10	0.23	97.7

(a) The collector was tetradecylamine HCl, 20 gpl in isopropanol.

A series of experiments then was conducted to investigate the effect of chromium concentration and reagent consumption at various concentrations. Data obtained from three experiments in the small glass cell with starting solutions containing 1, 10, and 100 ppm chromium are shown in Table 9. These data show--as expected--that more efficient removal of chromium was obtained in more concentrated solutions. (Note greater amounts of chromium per mg of collector added were removed at the higher concentrations.) Also of importance was that residual chromium concentrations could be reduced to a very low value (0.07 ppm chromium) if the starting solution was sufficiently dilute.

TABLE 9. FLOTATION DATA ON CHROMIUM-CONTAINING SOLUTIONS AT VARIOUS INITIAL CONCENTRATIONS

Initial Chromium Concentration[a], ppm	Amount of Collector Added[b], cc	Final Chromium Concentration, ppm	Indicated Percent Removal	Removal Efficiency, mg Cr/mg Collector
1	1.0	0.13	87	0.013
	2.0	0.07	93	0.007
10	1.0	3.72	63	0.094
	2.0	1.27	87	0.065
	3.0	0.87	91	0.046
100	2.0	77.0	23	0.173
	4.0	54.5	45	0.171
	6.0	32.0	68	0.170
	8.0	20.0	80	0.150

(a) Initial solution volume was 300 cc; pH at 6.0.
(b) Collector was tetradecylamine HCl, 20 gpl in isopropanol.

Because the removal efficiency is a major factor in determining the economics of the process, additional data were obtained on this variable for each of the three primary amine flotation collectors. These additional experiments were conducted in the Denver laboratory flotation cell shown previously in Figure 3. Flotation runs were made with 1-liter volumes of solution containing either 10-ppm or 100-ppm hexavalent chromium. The results obtained during these runs are summarized graphically in Figures 5 and 6 in which the weight of chromium removed is plotted against the weight of collector added. The removal efficiency at any point during the extraction can be determined by calculating the slope of the particular curve under consideration. In this manner, the maximum removal efficiency was found to be about 0.27 mg of chromium removed per mg of C_{14} amine added. This value was close to that predicted based on a reaction between the amine and dichromate ions; thus, the attainment of a higher removal efficiency even in large-scale equipment was, therefore, believed unlikely. It also should be noted that these data show a somewhat lower efficiency if other amine collectors are used or if the extraction is conducted to a point where very dilute chromium solutions are encountered.

Regeneration. The need for study of possible regeneration procedures arose from the fact that high extractions of chromium had been demonstrated during the experimentation, but that the efficiency of extraction was such that the process would be uneconomical for certain applications. The relatively high cost of the primary amine collectors, which were the only collectors found suitable for removal of hexavalent chromium,

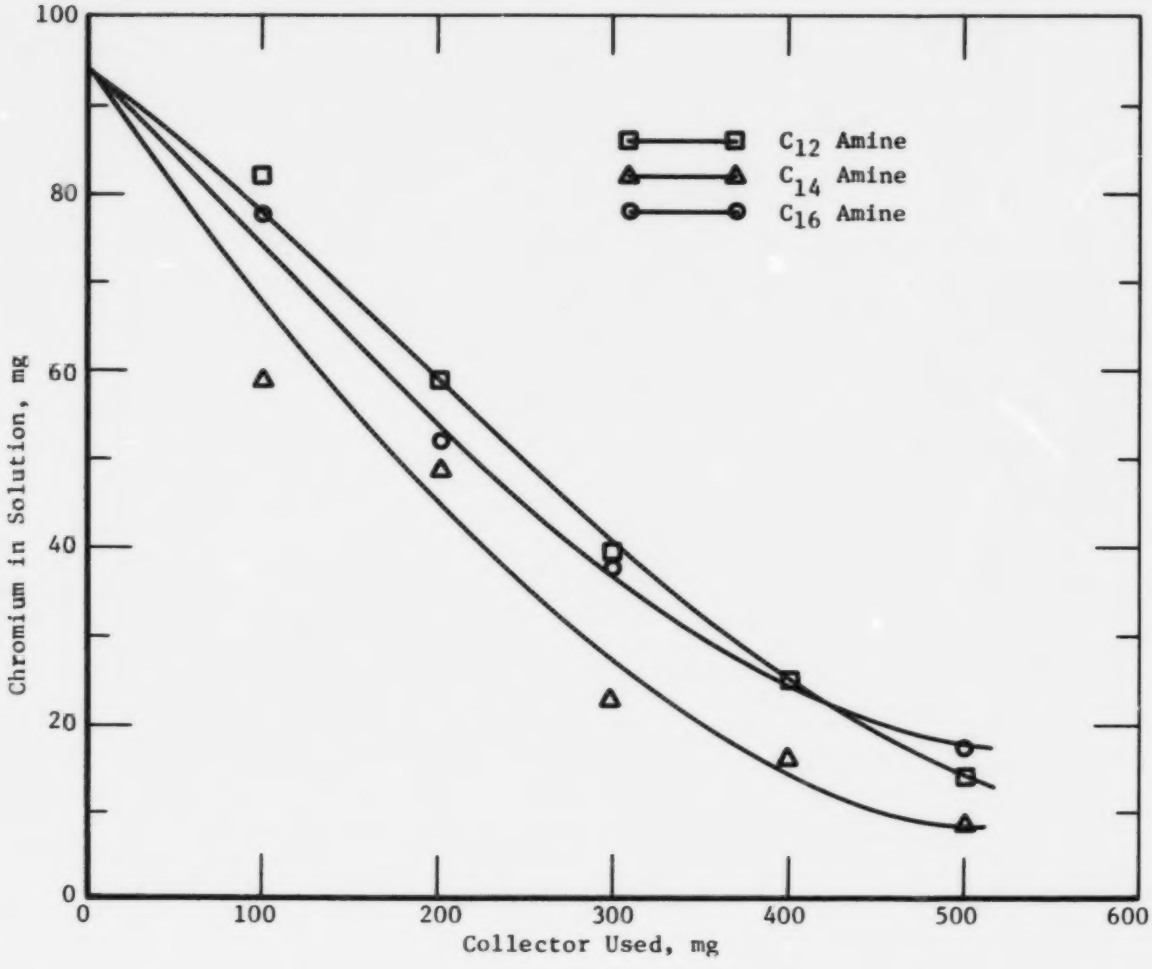


FIGURE 5. EFFICIENCY OF VARIOUS COLLECTORS FOR CHROMIUM REMOVAL FROM 100-ppm SOLUTION

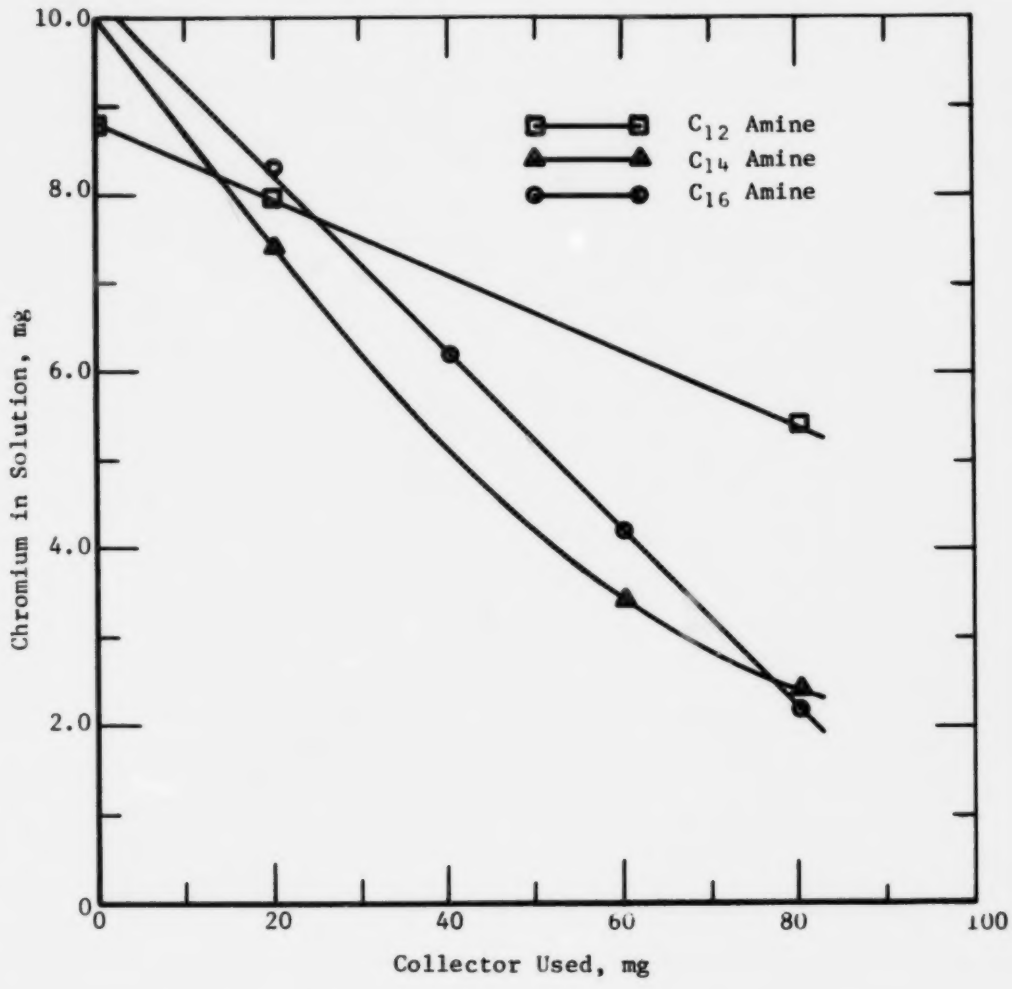


FIGURE 6. EFFICIENCY OF VARIOUS COLLECTORS FOR CHROMIUM REMOVAL FROM 10-ppm SOLUTION

indicated that the recovery and reuse of these collectors was mandatory. In order to make a valid evaluation of the process economics, a brief study was made of possible regeneration procedures which could be included in the process. The regeneration procedures which were considered included the use of strong acid or dilute caustic for treatment of the recovered spent flotation collector containing hexavalent chromium.

The initial experiments with acid regeneration, however, indicated that this method was not feasible. Although hexavalent chromium was liberated from the amine collector by acid treatment, the recovered amine was evidently degraded and did not remove chromium during a subsequent flotation cycle.

In subsequent experiments, effective regeneration was obtained by treatment of the flotation collector with dilute caustic solution. The caustic solution apparently liberated chromate from the precipitated complex of primary amine and chromic acid, and freed the amine which could be filtered and reused for subsequent flotation.

Experimental data shown in Table 10 illustrate the general results obtained with dilute caustic regeneration when applied after flotation of chromium from a 100-ppm solution with a C_{14} amine as collector. During this experiment, the entire spent flotation collector was recovered as completely as possible, regenerated with caustic, and reused for a total of three flotation/regeneration cycles.

The results shown indicate a loss of flotation efficiency after two regenerations (apparent percent removal decreased from 90 to 61), but almost complete recovery of hexavalent chromium. This decreased efficiency probably was due to decreased amounts of collector available during subsequent flotation cycles since about 60 percent of the initial collector was lost after three regenerations. The causes of reagent losses in the small-scale experimentation were not determined. It is possible that the amine was sufficiently soluble in water to permit some losses to the aqueous phase during the flotation cycles. The loss of materials in handling the small quantities of reagents involved in bench-scale experiments and the incomplete separation of phases also are possible routes for the decreased amounts of collector available in succeeding cycles. An accurate measure of the efficiency of reagent utilization can be obtained only by larger scale, continuous experimentation.

Chromium Removal (Trivalent). A possible alternative method for treating chromium-bearing effluents by ion flotation also was studied during the program. Basically, this technique involved the reduction of hexavalent chromium to the trivalent form and the subsequent removal of the trivalent chromium as hydroxide. The removal of the hydroxide by flotation might be more economical than removal of hexavalent chromium since the flotation could be effected with less costly collectors eliminating the need for possible regeneration procedures. The method is essentially the same as that used in large plating plants except that the chromium hydroxide is removed by sedimentation and clarification. For treatment of dilute rinse waters, especially, the flotation technique may have some advantage over sedimentation.

TABLE 10. EXPERIMENTAL DATA ON THE REGENERATION AND REUSE OF FLOTATION COLLECTOR FOR HEXAVALENT CHROMIUM

	Collector Weight, mg	Solution Data				Apparent Percent Chromium Removal	Apparent Percent Chromium Recovery
		Volume, cc	Initial Chromium, ppm	Final Chromium, ppm	Extracted Chromium, mg		
Cycle 1							
Flotation	500	1000	100	10	90	90	
Regeneration	(a)	170(b)	0	500	85.0		94
Cycle 2							
Flotation	(a)	1000	100	17	83	83	
Regeneration	(a)	170(b)	0	485	82.5		99
Cycle 3							
Flotation	(a)	1000	100	39	61	61	
Regeneration	214.7	170(b)	0	330	56.1		92

(a) Collector present in froth was recovered entirely after each flotation run and reused in subsequent cycles.

(b) The regeneration solution was 1 percent NaOH.

A brief series of experiments on the flotation of trivalent chromium showed that this form of chromium could be removed effectively by introducing a neutralized-fatty-acid collector such as potassium laurate. Typical data illustrating this result are shown in Table 11. As shown, the procedure was effective in removing up to about 95 percent of the chromium at pH 9.0. In one instance the chromium content of the solution was decreased to 0.6 ppm.

TABLE 11. FLOTATION DATA ON SOLUTIONS CONTAINING TRIVALENT CHROMIUM(a)

Expt. No.	Initial pH	ppm Cr^{+3}		Indicated Percent Removal
		Initial	Final	
22A	5.0	100	N.A.	0
22B	7.0	100	12.9	87.1
22C	9.0	100	5.3	94.7
22D	11.0	100	N.A.	0
25A	7.0	10	2.1	79
25B	9.0	10	0.6	94
25C	10.9	10	1.4	86

(a) Experiments were conducted by adding 0.2 cc of a solution containing 10 gpl of potassium laurate collector to 300 cc of initial chrome solution.

N.A. = Not analyzed (These final solutions showed no apparent extraction and were therefore not analyzed.)

Activated-Carbon-Adsorption Studies

General Description of Method. During the search of the literature for the state-of-the-art review, references were found in which the use of activated carbon for the adsorption of chromium from solution was cited. Activated carbon has been studied by various investigators for the tertiary treatment of domestic wastewaters. It also has been used for the adsorption of various materials from solution, including metal ions. For these reasons it was concluded that adsorption on activated carbon should be one of the techniques to be evaluated during this phase of the program.

Modern theories hold that the adsorption of materials from solution by activated carbon is accomplished by "van der Waal" or "dispersion" forces. These forces exist among all molecules and atoms, whether or not they are chemically combined, and may be compared to the gravitational force the earth exerts upon objects near it.

The ability of activated carbon to adsorb a given material depends largely on its surface area. Each particle of activated carbon has a vast interconnecting network of many-sized pores, providing a very large surface area for adsorption. Consequently, the pore structure of activated carbons is extremely important in determining their adsorptive properties.

Although the reasons are not completely understood, it is known that other substances have an influence on the adsorptive properties of activated carbons. Oxygen combined with the carbon can be particularly important and can increase its affinity for polar compounds and decrease its affinity for nonpolar compounds. In some cases, the inorganic-ash portion of the carbon can also influence the adsorption process. These latter factors may play a major role in the adsorption of inorganic materials.

Activated carbons are usually classified according to their physical form (e.g., powdered or granular) and according to their use (e.g., water grade, decolorizing, liquid phase, or gas phase). Granular carbons are those materials which are over 150 mesh in particle size and powdered carbons are those which are smaller in particle size.

Activated carbons are produced from various carbonaceous raw materials (e.g., bituminous coal, nut shells, lignite, pulp-mill residue, and wood). During this experimental program, many types and sizes of activated carbon were studied for the removal of chromium from waste solutions.

Equipment and Procedure. Preliminary Batch Experiments. In preliminary batch experiments on the adsorption of chromium, various amounts of carbon were mixed with a dichromate solution and the mixture was stirred for a predetermined time at room temperature. The mixture then was filtered on glass filter paper and the filtrate analyzed for hexavalent chromium.

During the preliminary batch experiments, several sizes of activated carbon, as well as those produced from various materials, were evaluated. The carbons studied are listed in Table 12.

Continuous Carbon Columns. In subsequent continuous-adsorption experiments, a series of four glass columns arranged as shown in Figure 7 was employed. The columns were constructed of 2-inch-diameter Pyrex glass tubing and were approximately 30 inches in length. By pumping the solution through the four columns in series, a total carbon-bed depth of 10 feet was attainable. The granular carbon was supported on a 65-mesh stainless steel grid. Oscillating pumps were used to pump the solution through the columns. The solution flow was down through the carbon. The columns were constructed with a sampling port at the bottom of each one so that effluent samples could be obtained for analysis. The type carbon selected for the continuous experiments was Pittsburgh Activated Carbon Company's Type OL which is a granular carbon with a particle size of 20 x 50 mesh. This selection was based on the overall results of preliminary batch experiments.

TABLE 12. TYPES OF ACTIVATED CARBON EVALUATED

Trade Name	Company	Source Material	Type and/or Size
Nuchar	West Va. Pulp & Paper	Pulp mill residue	Granular (8 x 30) (WVL)
"	ditto	ditto	Pulverized
Pittsburgh	Pittsburgh Act. Carbon Co.	Bituminous coal	Pulverized (RC)
"	ditto	ditto	8 x 30 (SGL)
"	"	"	12 x 40 (CAL)
"	"	"	20 x 50 (OL)
Absorbite	Barneby-Cheney	Nut shells	Pulverized, nonactive (XB)
"	ditto	ditto	Granular nonactive (BB)
"	"	"	Pulverized, low-active (YD)
"	"	"	Granular, low-active, 12x30 (PA)
"	"	"	Pulverized, high-active (XZ)
"	"	"	Granular, high-active, 10x50 (PC)
"	"	"	Pulverized, acid wash (JF)
"	"	"	Granular, acid wash, 10x50 (PK)
Cliffchar	Royal Oak Charcoal Co.	Wood charcoal	Pulverized
"	ditto	ditto	Granular, 10 x 20

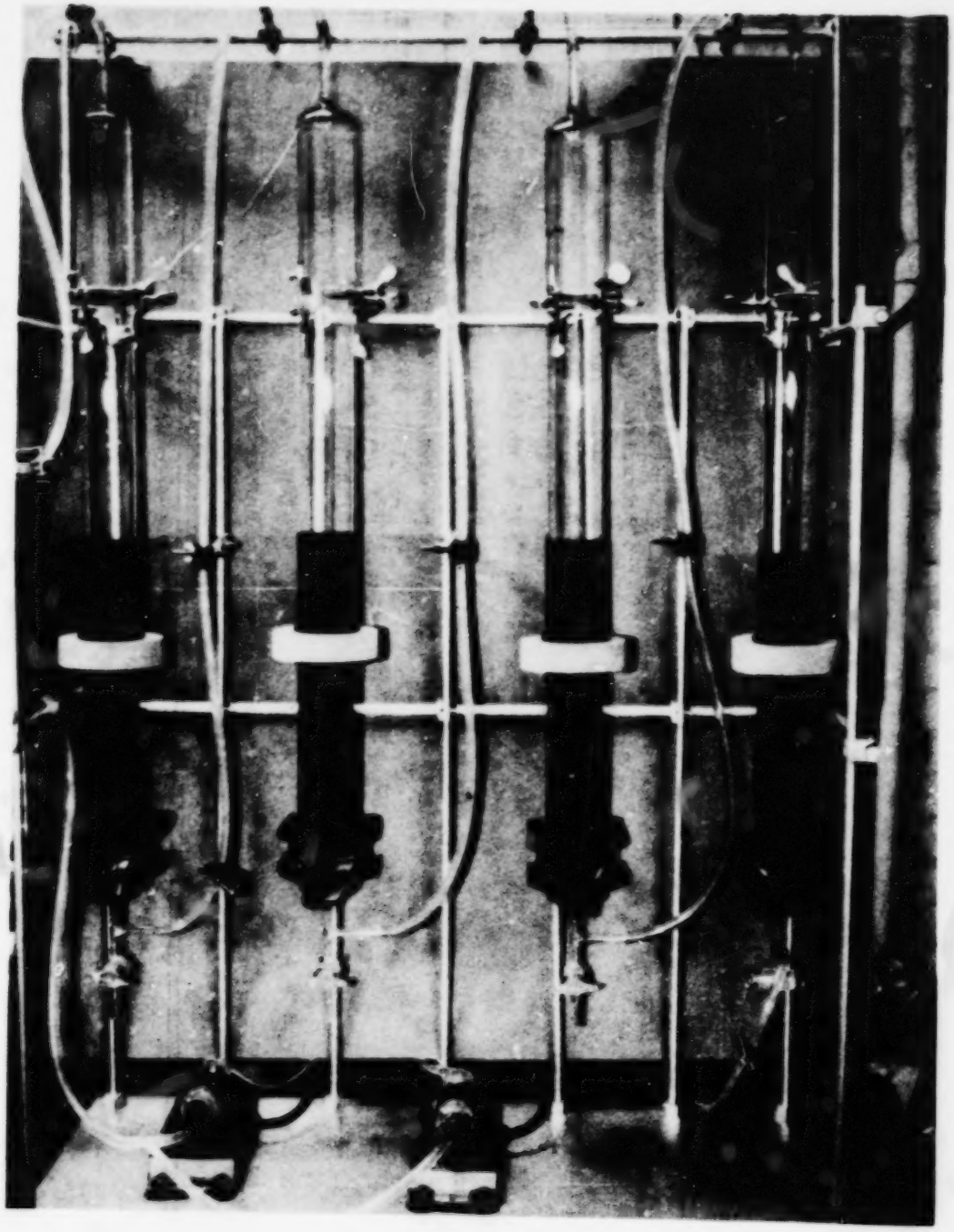


FIGURE 7. BENCH-SCALE CONTINUOUS COLUMNS FOR ADSORPTION EXPERIMENTS

The procedure used in the continuous experiments was to pump a synthetic waste solution containing varying amounts of chromium through the column at a given rate with periodic analysis of effluent samples. In some experiments only one column was used while in others two, three, or all four were used. In this manner the time of "breakthrough", when the effluent contained the element being adsorbed, could be observed as well as the time when the carbon was completely loaded. From the data collected during these experiments, the capacity of the carbon for adsorbing chromium could be determined. The major variables studied during these experiments were:

(1) pH of the feed solution
(2) Concentration of the feed solution
(3) Rate of flow or residence time
(4) Ionic form of the element in solution (e.g., dichromate, chromate, or chromic acid).

Results. Batch Experiments. A series of experiments to compare the effectiveness of various types of carbon was conducted in the initial stages of the study. The results are shown in Table 13. Carbons produced from nut shells and wood charcoal (e.g., Absorbite and Cliffchar) effected very little chromium removal. Those produced from pulp mill residue (Nuchar) adsorbed or removed approximately 50 percent of the chromium present in the solution. Carbon produced from bituminous coal (Pittsburgh) removed from 52 to 89 percent of the chromium.

To study some of the variables that could affect chromium removal (carbon, concentration time, pH), several additional series of experiments were conducted with Pittsburgh RC pulverized carbon. The results obtained on the effect of carbon concentration are shown in Figure 8. When the concentration was increased to 35 grams per liter, the percentage removed reached 94 percent and appeared to level out since a further increase to 40 grams per liter did not increase the amount of chromium removal.

The effect of contact time on chromium adsorption was determined by contacting a solution containing 10 ppm chromium with 10 gpl of carbon for varying periods up to 2 hours. Results, shown graphically in Figure 9 indicate that maximum adsorption occurred within the first 10 minutes and that increasing contact time beyond this point had very little effect.

The effect of pH value on chromium adsorption is shown in Figure 10. The normal pH value of the synthetic waste solution containing 10-ppm chromium as dichromate using distilled water is 6.0. During this series of experiments, the pH value was varied from 2 to 12 by the addition of either sodium hydroxide or sulfuric acid. The results indicated that low pH values were required for effective chromium removal.

Laboratory experiments also were conducted to determine the maximum adsorptive capacity of various carbon samples at chromium concentrations between 10 and 2000 ppm. Typical data obtained in these experiments are

TABLE 13. REMOVAL OF HEXAVALENT CHROMIUM WITH VARIOUS TYPES OF ACTIVATED CARBON

Type of Activated Carbon	Physical Characteristics	Apparent Percent Chromium Removal(a)
Pittsburgh - RC	Pulverized	89
Pittsburgh - OL	Granular (20 x 50 mesh)	80
Pittsburgh - CAL	Granular (12 x 40 mesh)	67
Pittsburgh - SGL	Granular (8 x 30 mesh)	52
Nuchar - Aqua A	Pulverized	50
Nuchar - WVL	Granular (8 x 30 mesh)	47
Absorbite - XB	Pulverized (nonactive)	12
Absorbite - BB	Granular (nonactive)	26
Absorbite - YD	Pulverized (low-active)	14
Absorbite - PA	Granular (low-active, 12 x 30)	17
Absorbite - XZ	Pulverized (high-active)	19
Absorbite - PC	Granular (high-active, 10 x 50)	19
Absorbite - JF	Pulverized (acid washed)	17
Absorbite - PK	Granular (acid washed, 10 x 50)	17
Cliffchar	Pulverized	6
Cliffchar	Granular (10 x 20 mesh)	10

(a) In all cases, the experimental conditions were 10-gram - per-liter carbon concentration and 5-minute contact time.

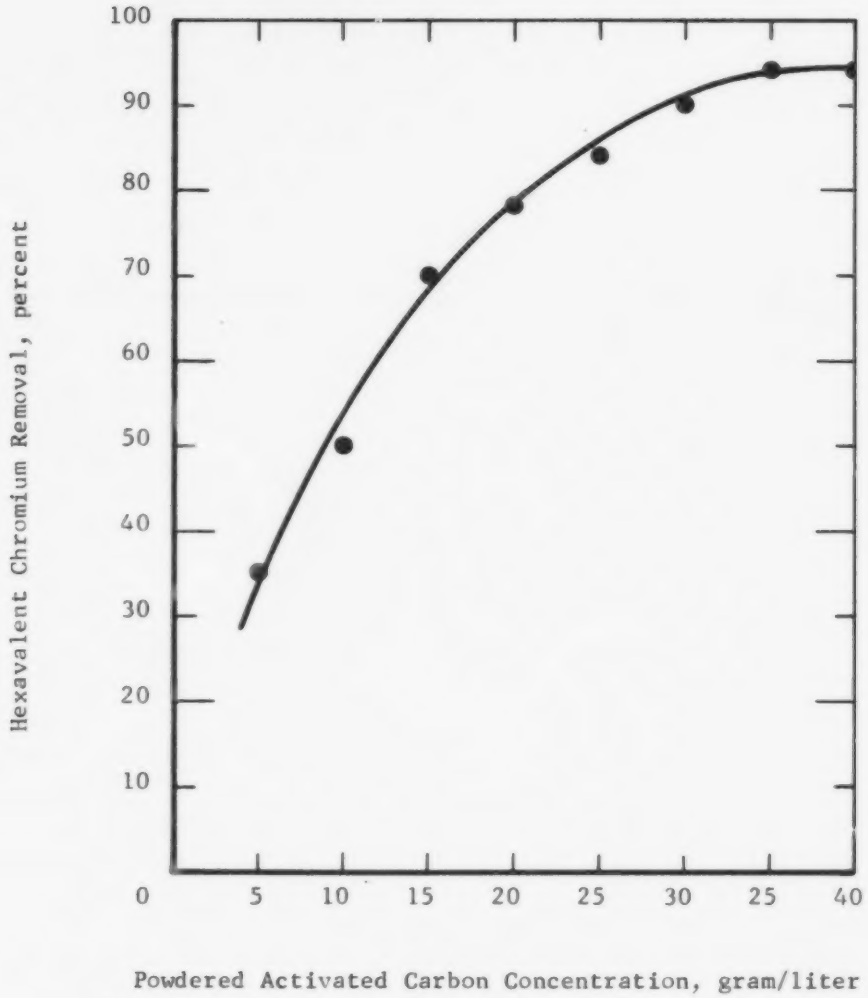


FIGURE 8. AMOUNT OF POWDERED ACTIVATED CARBON REQUIRED FOR HEXAVALENT CHROMIUM REMOVAL

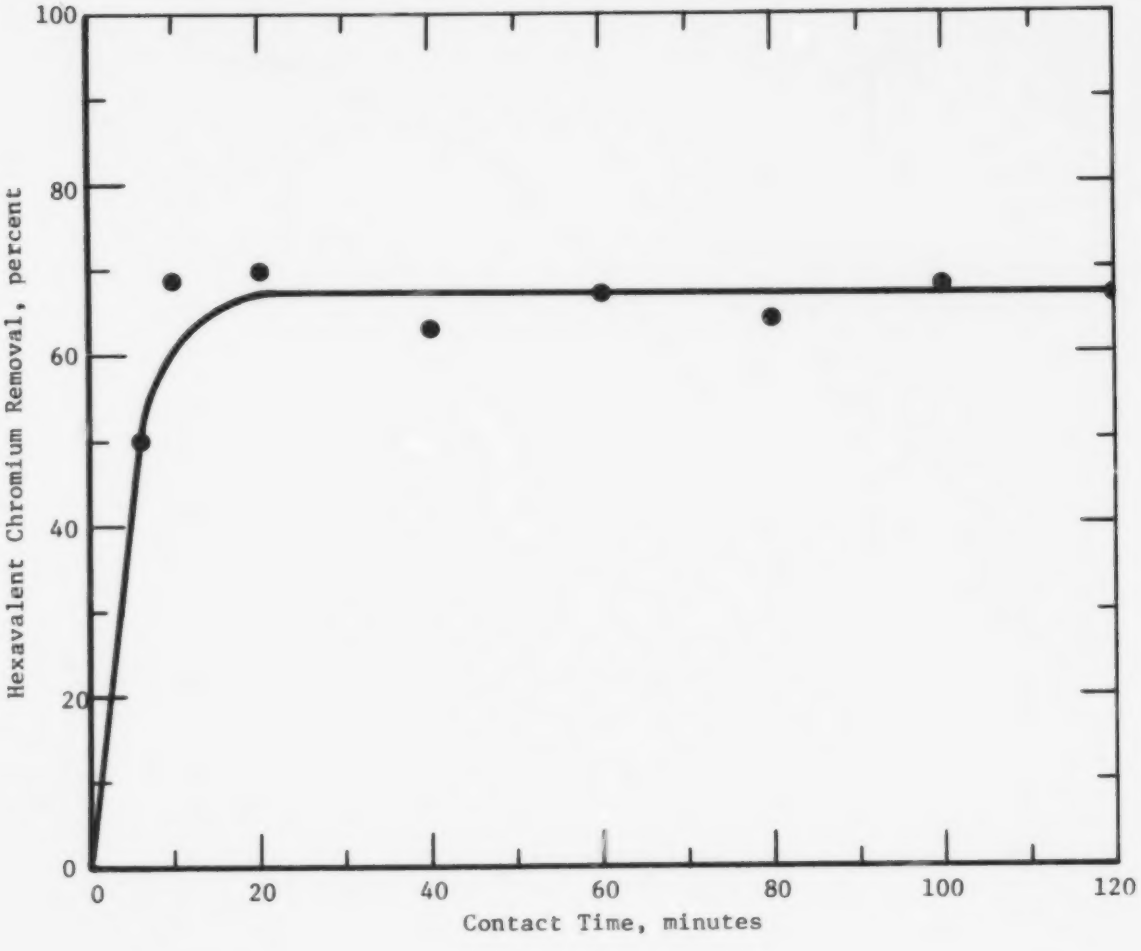


FIGURE 9. EFFECT OF CONTACT TIME ON CHROMIUM REMOVAL

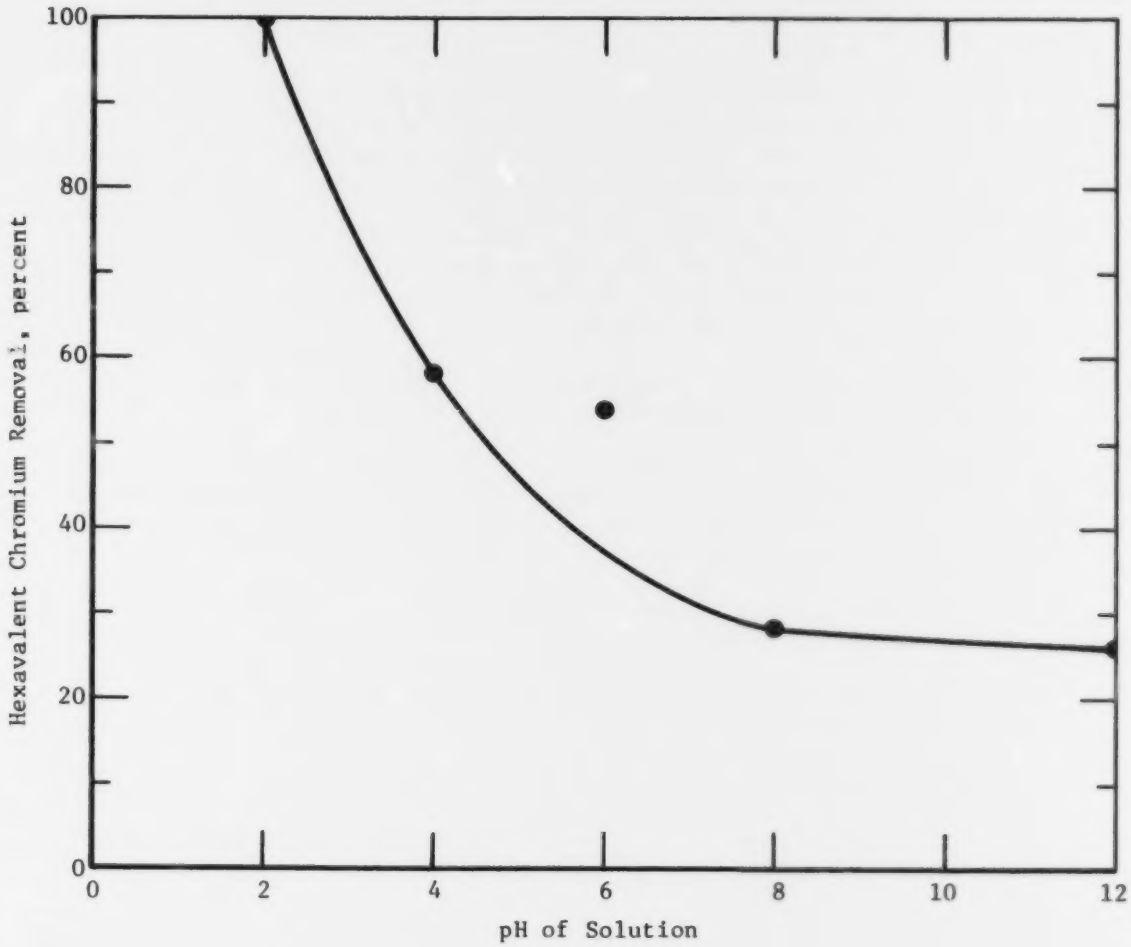


FIGURE 10. EFFECT OF pH ON CHROMIUM REMOVAL

shown in Figure 11. These data show adsorption isotherms (equilibrium adsorption capacities versus solution concentration) for the two types of carbon which gave the best results. The isotherms shown in this figure are important in selecting the best carbon for a specific application. For example, at high concentrations of about 2000 ppm, both carbons have identical capacities; thus, the selection would be based on carbon cost. In this case, Nuchar carbon would be selected since it is significantly cheaper than Pittsburgh OL carbon. On the other hand, the capacities of each carbon at low concentration are quite different. Pittsburgh OL, for example, has over twice the capacity of Nuchar at concentrations less than 70 ppm. Thus, Pittsburgh OL would be preferred in this case since the higher capacity more than offsets the higher unit cost.

In addition to comparative data, the isotherms show the ultimate adsorption capacities attainable with each type of carbon in a column system operated for single adsorption and disposal. Actual data points obtained in this series of experiments indicate capacities of up to 21 percent of the weight of carbon as chromium can be adsorbed at a feed concentration of 2000 ppm of hexavalent chromium. Operation at these concentrations is considered feasible if rinse water is recirculated in a closed loop around the rinsing tank. Thus, adsorption capacities of 20 percent might be practical in a commercial system.

In summary, the batch experimentation on the removal of hexavalent chromium from synthetic waste solutions indicated that

(1) Pittsburgh pulverized carbon, type RC, effects the largest percentage of chromium removal with Pittsburgh granular, type OL, being second best. The difference between the pulverized and granular carbon is almost insignificant (Table 14).

(2) Thirty-five grams of carbon per liter of waste solution adsorbs maximum amount of hexavalent chromium.

(3) No reduction of chromium occurs during carbon contact at pH values in the range of about 3 or greater.

(4) Maximum adsorption is obtained within 10 minutes.

(5) Low pH values (about 2 to 3) are required for effective chromium removal.

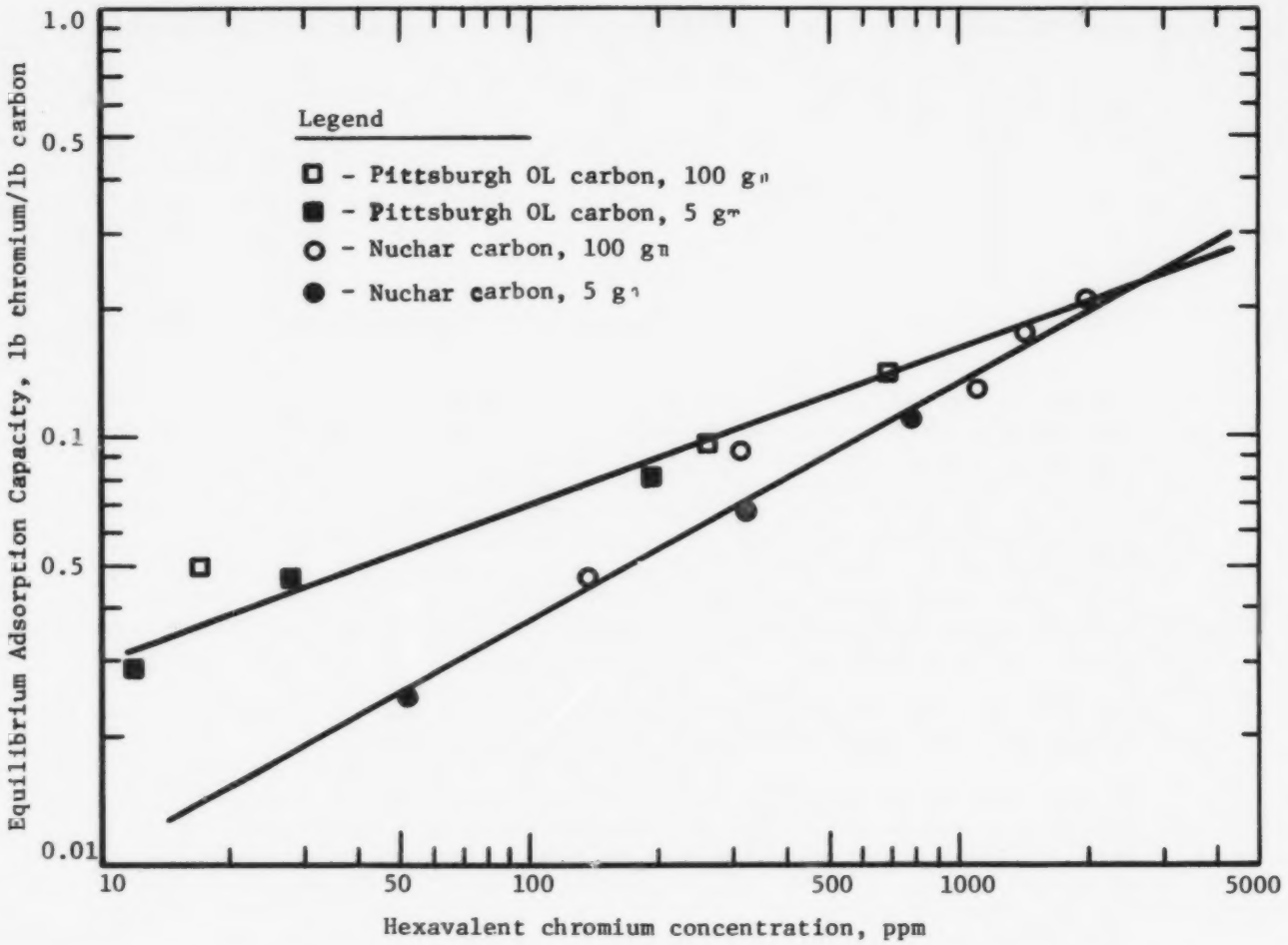


FIGURE 11. TYPICAL ADSORPTION ISOTHERMS FOR HEXAVALENT CHROMIUM

TABLE 14. COMPARISON OF GRANULAR AND PULVERIZED ACTIVATED CARBON FOR CHROMIUM REMOVAL AT VARIOUS CONCENTRATIONS

Carbon Concentration, grams per liter	Hexavalent Chromium Removed, percent	
	Pittsburgh Granular	Pittsburgh Pulverized
5	57	74
10	80	89
15	86	96
20	91	96
25	93	96
30	94	96
35	96	96
40	98	97

Continuous Carbon Columns. A total of ten experiments was conducted in a continuous fashion using one or more of the carbon columns shown in Figure 7. The simulated waste solutions fed to the columns contained 10, 100, and 1000-ppm chromium prepared from either dichromate or chromic acid. In the first seven experiments, distilled or deionized water was used to make up the solution. The last three experiments were conducted using tap water. The pH value of the feed solutions ranged from 1.8 to 6.3. Feed rates varied from 0.5 to 5.0 gallons per minute per square foot of bed surface area. These rates correspond to retention times from about 2 to 15 minutes.

The data in Table 15 show the conditions employed and the results obtained during the continuous experiments on chromium removal.

In the first experiment (1), all four columns were used. Each column was filled with 700 grams of type OL carbon. The feed solution was made up with distilled water and potassium dichromate and contained 10 ppm chromium at a pH value of 6.3. A total of 1324.8 liters of solution was fed at a rate of 0.5 gallon per minute per square foot of carbon surface area which gave a retention time of about 15 minutes. During this experiment 1.2 grams of the 1.3 grams of chromium fed were adsorbed primarily in the first column. This amounted to over 90 percent adsorption of the incoming chromium and gave a carbon-loading capacity of about 0.002 (weight of chromium per weight of carbon). This ratio was considerably better than that obtained in any of the batch experiments. Although only 92 percent was adsorbed on the first column, the other 8 percent was adsorbed by the following column. This experiment was discontinued since it was felt that solutions of higher concentration fed at faster rates would give the needed data more quickly.

In Experiment 2 all four columns were also employed. The solution concentration was increased to 100 ppm and the feed rate was increased to give a retention time of about 4 minutes. About 75 percent of the 15.5

TABLE 15. CONTINUOUS EXPERIMENTS ON ADSORPTION OF CHROMIUM WITH ACTIVATED CARBON

Expt. No.	No. of Columns Used	Feed Solution						Effluent				Total Chromium Adsorbed		Carbon Loading Capacity, Grams Cr/g Carbon
		Type[a]	Rate, gpm/ft^2	pH	Volume, liters	Chromium Content ppm	Chromium Content g	pH	Volume, liters	Chromium Content ppm[b]	Chromium Content g	g	%	
1	4	$K_2Cr_2O_7$	0.5	6.3	1324.8	10	1.3	>8.0	1324.8	0-2	≈0.13[c]	1.2	92.2	0.002
2	4	$K_2Cr_2O_7$	2.0	5.4	155.4	100	15.5	3-9	155.4	0-50	≈3.9[d]	11.6	74.8	0.017
3	1	$K_2Cr_2O_7$	2.0	2.1	291.4	100	28.5	2-7	287.1	0-30	5.6[e]	22.9	80.4	0.032
4[f]	1	$K_2Cr_2O_7$	3.0	4.0	203.5	100	20.4	2-7	203.5	0-50	4.2[e]	16.2	79.5	0.023
5[f]	1	$K_2Cr_2O_7$	3.0	4.0	18.9	100	1.9	>8.0	18.9	0-20	0.4[e]	1.5	79.0	0.002
6	1	$K_2Cr_2O_7$	3.0	4.0	18.9	100	1.9	6.8	18.9	0-10	--	38.0	95.8	0.055
		$K_2Cr_2O_7$	3.0	4.0	18.9	1000	18.9	6.8	18.9	0-10	0.3			
		$K_2Cr_2O_7$	3.0	2.5	18.9	1000	18.9	6.7	18.9	0-10	1.4			
				Totals	56.7		39.7		56.7		1.7[e]			
7[g]	1	CrO_3	5.0	1.8	94.6	1000	94.6	3-4	94.6	0-5	3.4[e]	91.2	96.4	0.125
11[g]	1	CrO_3	5.0	2.0	83.3	1000	83.3	3-4	83.3	0-1	5.5[e]	77.8	93.4	0.111
13[g]	1	CrO_3	5.0	3.0	323.8	100	32.4	2-3	323.8	0-2	1.9[e]	30.5	94.0	0.043
14[g]	1	CrO_3	5.0	2.8	372.2	100	37.2	3-4	372.2	0-4	4.4[e]	32.8	88.1	0.048

(a) Synthetic solutions were made with reagent-grade chemicals as follows: $K_2Cr_2O_7$ = potassium dichromate, CrO_3 = chromic acid.

(b) Concentration is given in range of ppm chromium.

(c) Estimated by assuming average chromium content of effluent was 1 ppm.

(d) Estimated by assuming average chromium content of effluent was 25 ppm.

(e) Based on actual analyses.

(f) This experiment was conducted using a different column of carbon than had been used previously.

(g) The feed solution for these experiments was made from tap water instead of distilled or deionized water used previously.

Conditions: Carbon content, 700 grams per column, 2800 grams in four columns.

grams of chromium fed during this run was adsorbed to give a carbon loading capacity of 0.017. The increased capacity was believed due to operation at a lower pH (5.4) and a higher chromium concentration.

The following two experiments (3 and 4) were conducted using only one of the columns. The pH value in these experiments was 2.1 and 4.0, respectively, and the retention time was 4 and 3 minutes. In both cases about 80 percent of the chromium fed was adsorbed on the carbon. The carbon-loading capacities were even better than in the two initial experiments (i.e., 0.032 and 0.023).

Experiment 5 was conducted using the same conditions except that the column was loaded with fresh carbon. This experiment was terminated due to the high chromium content (8 to 10 ppm) of the effluent. It was believed that, since the carbon had not been washed with acid previously, any basic materials present in the carbon caused the pH value of the solution to increase to a value greater than 8. It was theorized that by prewashing the carbon with acid these basic materials would be leached out.

In Experiment 6, three different feed solutions were used (100 ppm, pH 4; 1000 ppm, pH 4; and 1000 ppm, pH 2.5). A total of 38 grams of the 39.7 grams of chromium fed was adsorbed on the carbon. This amounted to about 96 percent adsorption and a chromium to carbon ratio of 0.055. This experiment appeared to confirm the previous finding that the adsorptive capacity of the carbon increases with increased concentration of hexavalent chromium in the feed and with lower pH values.

The next two experiments (7 and 11) were conducted to determine the maximum capacity of the carbon while feeding a solution containing 1000 ppm Cr. From the data in Table 15 it can be seen that with low pH values and a high chromium concentration in the feed solution, the capacity reached much higher levels (chromium to carbon ratios of 0.125 and 0.111, respectively) with excellent removal efficiency (95 percent).

In Experiments 13 and 14 the column was operated under conditions which would be practical in a commercial-scale unit. After the effluent contained 1 ppm chromium, the experiment was stopped, the carbon was regenerated, and a second adsorption cycle conducted (Run 14). The adsorption efficiency for chromium in this second cycle by the regenerated carbon was apparently unimpaired.

These final experiments indicated that, with waste solutions containing as high as 1000 ppm chromium and at pH values of 4 or less, virtually all of the chromium could be adsorbed. They also indicated that it is possible to load the carbon with at least 10 percent of its weight of chromium.

Regeneration. During the experimentation on the adsorption of chromium on activated carbon, various techniques were studied to regenerate the carbon for reuse. Several types of regenerants at various concentrations were tried. These regenerants were

(1) Sodium hydroxide (NaOH)
(2) Sulfuric acid (H_2SO_4)
(3) Hydrochloric acid (HCl)
(4) Water (H_2O)
(5) Acetic acid (CH_3COOH).

Table 16 shows the conditions and results of the experiments on regeneration of carbon and recovery of chromium. The data indicated that

(1) Both sodium hydroxide and sulfuric acid were effective regenerants. Used alone, sulfuric acid was capable of removing all of the adsorbed chromium (Experiment 4). When sodium hydroxide was used alone, the rate of chromium removal from the carbon became low after about two-thirds of the chromium was extracted (Experiments 1, 6, 7, 11).

(2) Regeneration by means of sulfuric acid results in the reduction of hexavalent chromium to trivalent chromium (Experiments 3, 4, 6, 7, 11). If chromium recovery were desired, sulfuric acid therefore would not make a suitable regenerant. However, for simple disposal, acid regeneration might be feasible since trivalent chromium must be produced prior to disposal.

(3) Regeneration by sodium hydroxide leaves the chromium in the hexavalent state as sodium chromate possibly suitable for recovery.

(4) Regeneration of the carbon with either acid or sodium hydroxide appeared to be a technically feasible method of operation. This is borne out by the fact that the partially regenerated carbon from Experiment 13 was reused with no observable impairment in efficiency. It was suspected, however, that numerous cycles of regeneration and reuse might significantly affect the adsorption efficiency of the carbon, and should be investigated in subsequent studies.

(5) The maximum concentration of chromium possible in the regenerating solutions remained to be established. In the laboratory work, concentration ratios of 25:1 were obtained, with evidence that much higher ratios may be possible.

TABLE 16. REGENERATION OF CARBON FROM CHROMIUM ADSORPTION EXPERIMENTS

Expt. No.	Chromium Adsorbed on Carbon, g	Regeneration Solution, Type[a]		Volume Used, liters	Chromium Recovered by Regeneration, Grams	Chromium Recovered by Regeneration, Percent of Cr Fed	Grams of Regenerant Required/ Gram of Cr
1	1.2	1% NaOH		12.9	0.79	65.8	129
		-- H_2O		6.0	0.15[b]	12.5	--
		1% H_2SO_4		1.0	0.12[b]	10.0	83
			totals	19.9	1.06	88.3	

TABLE 16. (Cont.)

2	11.6	10% H_2SO_4		18.4	9.41[b]	81.0	195
3	22.9	10% H_2SO_4		18.0	19.1[b]	83.4	94
4	16.2	10% H_2SO_4		7.0	16.3[b]	100.0	43
5	1.5	10% NaOH		4.0	1.7	100.0	235
6	38.0	1% NaOH		8.3	27.5	72.3	3
		5% H_2SO_4		4.0	10.5[b]	27.7	19
			totals	12.3	38.0	100.0	
7	91.2	1% NaOH		11.5	60.5	66.4	2
		5% H_2SO_4		8.5	27.0	29.6	16
			totals	20.0	87.5	96.0	
11	77.8	1% NaOH		17.0	51.0	65.6	3
		5% H_2SO_4		11.7	18.5[b]	23.8	32
		5% HCl		1.8	0.2	0.2	450
		20% CH_3COOH		6.0	0.4	0.4	300
			totals	36.5	70.1	90.0	
13	30.5	1% NaOH		5.9	15.3	50.2	4
		0.8% H_2SO_4		7.1	4.6	15.3	13
			totals	13.0	19.9	65.5	
14	32.8	1% NaOH		5.1	13.3	40.6	4
		— H_2O		18.7	5.3	16.1	--
			totals	23.8	18.6	56.7	

(a) NaOH = sodium hydroxide, H_2O = water, H_2SO_4 = sulfuric acid, HCl = hydrochloric acid, CH_3COOH = acetic acid.

(b) Recovered as reduced chromium.

Liquid-Liquid Extraction Studies

General Description of Method. The liquid-liquid extraction process as it might be applied to metal-finishing wastes is shown in Figure 12. The waste or aqueous phase follows the solid line path through the system into the first-stage mixer (Item 2 in the diagram) then to the first-stage settler (4). Here the phases separate and the aqueous phase now partially depleted of its contaminant passes through the second-stage mixer and settler (5 and 3) where virtually all the remaining contaminant is removed. The organic phase containing the extracting compound passes through the two-stage extraction system countercurrent to the aqueous phase along the path indicated by the dashed lines through the two stages of mixing and settling (5, 3, 4, and 8).

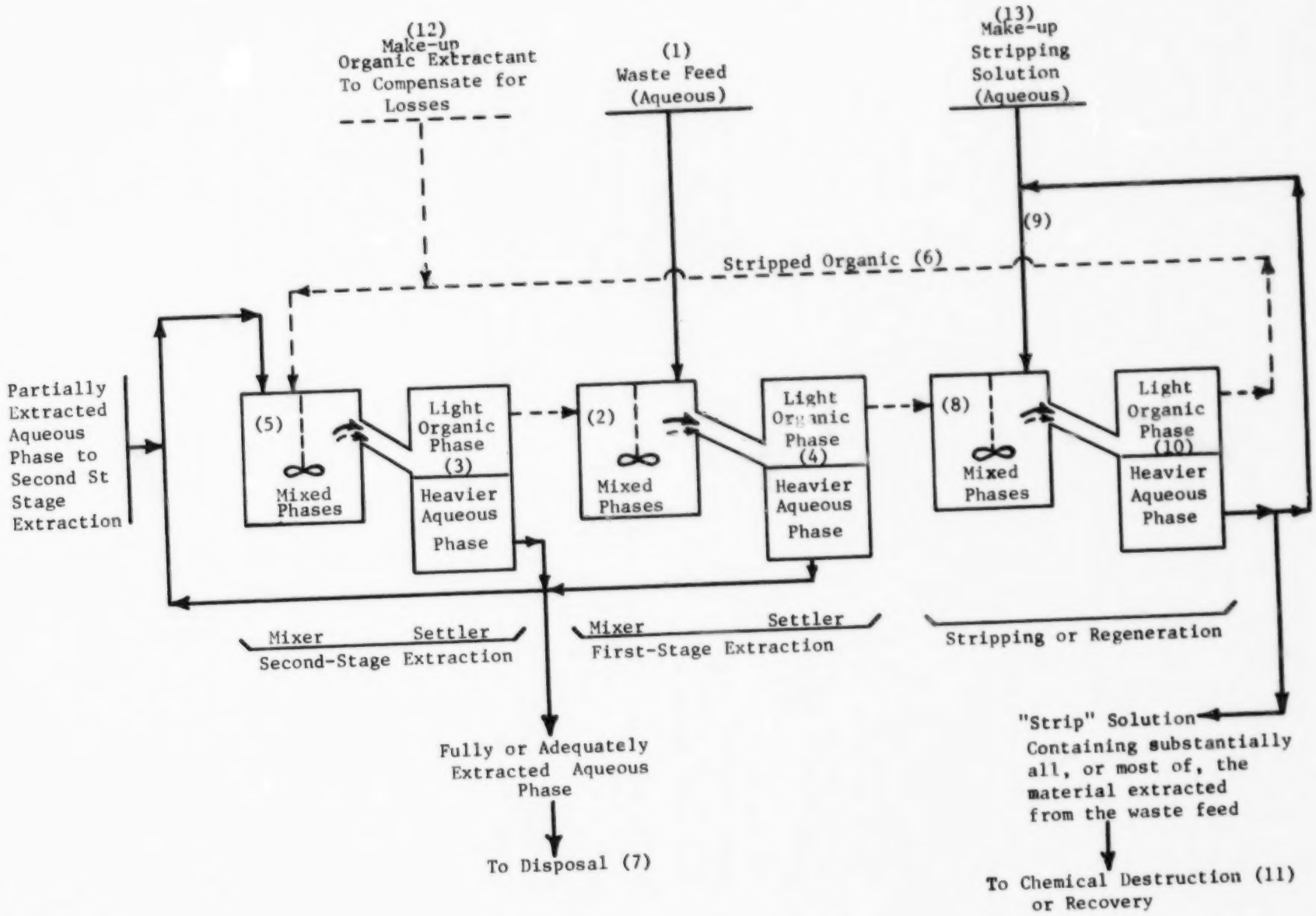


FIGURE 12. EXAMPLE OF TWO-STAGE EXTRACTION, SINGLE-STAGE STRIPPING LIQUID-LIQUID EXTRACTION PROCESS

As it issues from the settler (4) it is sent to a regeneration stage (8 and 9) where it is stripped of its load of contaminant and restored to its original composition. The regenerated organic material is then recycled back to the extraction stage (6). In the stripping or regeneration section, the stripping agent is constantly recirculated through the mixer-settler (8 and 10). Periodically, enough of the stripping solution now loaded with the contaminant is removed from the circuit for subsequent treatment (11).

The process outlined in Figure 12 is merely an example. Numerous variations in flow patterns, number of stages, etc., are possible.

Equipment for liquid-liquid extraction too can be varied. The equipment implied in Figure 12 is the so-called horizontal type, mechanically agitated mixer-settler, in which in each stage the phases are intimately dispersed in one vessel by agitation and then permitted to flow by gravity to another settling vessel for phase separation. Each stage, therefore, requires two separate vessels. Other types of mechanical mixer-settlers may be used. These include the vertical type in which the stages are superimposed in a single vertical shaft with a central axle for driving the agitators in each mixing section and baffled tanks similar in nature to the apparatus used in the laboratory. There are several other types of liquid-liquid extraction equipment which probably also would be applicable to the treatment of metal-finishing waste. These include

(1) Various types of columns in which no agitation is employed, such as perforated plate columns, bubble cap columns, packed columns, and spray columns. This apparatus might possibly be applicable to the treatment of metal-finishing wastes.

(2) Mechanically agitated columns, such as the so-called pulsed column. These would be applicable to the treatment of metal-finishing wastes also, but would be more costly than spray columns.

(3) Centrifuge types in the contacting or mixing. Settling is greatly accelerated making possible high treatment rates and consequently reduced equipment sizes. These types generally are expensive, but require less floor space than the other types.

Chemistry of Liquid-Liquid Extraction. The chemistry involved in liquid-liquid extraction can probably be most clearly explained by an example. For the extraction of hexavalent chromium, a number of organic compounds would be satisfactory. The one investigated most thoroughly in the laboratory campaign was the so-called Alamine 336, manufactured by General Mills. Another which was investigated to a lesser extent, but which exhibited as much promise, was Amberlite LA1, manufactured by Rohm and Haas. The former is a tertiary amine, the latter a secondary amine.

These amines have the capacity for reacting with hexavalent chromium in acidic solution by the following mechanism.

$2R_3N$	+	Cr_2O_7 =	+	$2H^+$	→	$(R_3NH)_2Cr_2O_7$
Alamine 336		Dichromate ion as would exist in acidic chromium rinses		Hydrogen ions as obtained in acidic conditions		Compound of amine with dichromate
↑						↑
Soluble in kerosene or other solvents; very low or negligibly soluble in water; generally used in dilute solution in kerosene, etc., at strengths up to about 5 percent						Soluble in kerosene or other organic solvents; low or negligible solubility in water; remains dissolved in the organic phase after separating

Another possible mechanism is to first convert the amine to an amine sulfate and then react it with the chromium solution; but the overall effect, the conditions required, etc., do not vary significantly from those exhibited in the above reaction.

After the reaction of chromium with the amine is completed in the mixing section of the extraction equipment and the phases are separated, the chromium compound with the amine preferentially dissolved in the organic phase is removed from the system to be stripped. In the stripping operation, the aim is to remove the chromium from combination with the amine into a highly concentrated aqueous phase and to restore the amine to its original composition so that it can be recirculated to extract chromium from additional waste solution. Where the extraction of chromium from the waste solution requires an acidic condition, the stripping reaction requires an alkaline condition. Stripping takes place according to the following reaction:

$(R_3NH)_2Cr_2O_7$	+	4NaOH	→	$2Na_2CrO_4$	+	$2R_3N$	+	$3H_2O$
Compound of amine with dichromate dissolved in organic phase		Sodium hydroxide in aqueous stripping solution		Sodium chromate dissolved in aqueous solution after stripping; may be recirculated to build Cr content to 10 or 20 g/l		Alamine 336 dissolved in kerosene after stripping; recycled to additional extraction		Water

Requirements for Feasibility. For liquid-liquid extraction to be feasible in the treatment of metal-finishing wastes, these conditions would have to be met:

(1) The extraction of chromium from rinse waters should be virtually complete. Although there may at present be a certain laxity in legislation and enforcement, the day may come when every plater may be required to satisfy limits as low as 1 or 2 ppm of chromium. An acceptable liquid-liquid extraction process would have to be capable of achieving such limits.

(2) Reagent recovery by stripping should be efficient.

(3) The stripping operation should produce a greatly concentrated solution of the contaminant either for recovery or chemical destruction.

(4) The treated effluent solution should be sufficiently free from organic contaminants such as oil to satisfy local restrictions. Present restrictions on oil are variable, ranging from zero to some nonspecific quantity described in such terms as "none making the water unsuitable for the use indicated". It is the very nature of liquid-liquid extraction in which oily substances, such as kerosene, are intimately dispersed in the waste, to introduce some oil into the water phase. The process should operate, therefore, in such a manner that the "oily substance" content of the discharged waste is within permissible limits. The control of the oil content of the treated effluent might be important if the water were reused, even in part, for rinsing, owing to the possible effects on work quality.

(5) The operation should be relatively simple and routine requiring a minimum of time and attention by the plater.

(6) Costs, both capital and operating, should be reasonable.

In the following sections of this report, the feasibility of liquid-liquid extraction for chromium removal is discussed on the basis of the data obtained in the experimental program.

Equipment and Procedure. Preliminary batch experiments were made in separatory funnels, by the conventional single-stage procedure. In these runs, measured quantities of the aqueous and organic phases adjusted to the desired pH level were mixed. The mixture was permitted to stand for 20 minutes to effect phase separation, and the treated aqueous phase was analyzed to determine its metal content.

Subsequent mixer-settler runs were made in the apparatus shown in Figure 13, which provided three stages of extraction, with the aqueous phase being fed into the righthand mixing compartment. Agitation by laboratory stirrers was provided in each stage. The treated aqueous solution was overflowed from the lefthand settling compartment and the "loaded" organic was aspirated by suction from the righthand settling compartment.

The runs were made at various flow rates, volumetric ratios of aqueous to organic, and composition of aqueous and organic solutions.

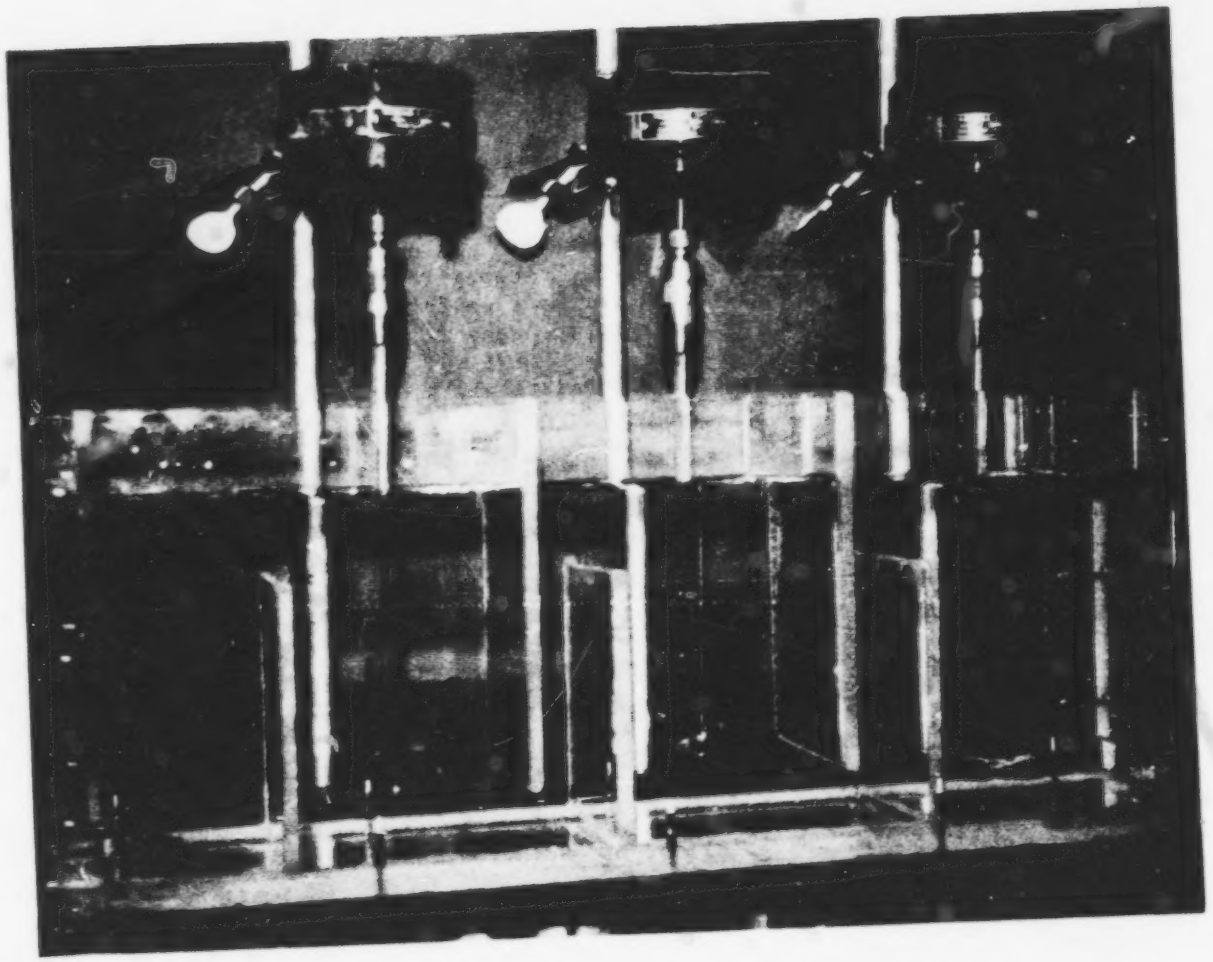


FIGURE 13. BENCH-SCALE MORRIS-TYPE CONTACTOR FOR CONTINUOUS LIQUID-LIQUID EXTRACTION EXPERIMENTS

Results. The program was designed to determine how well the liquid-liquid extraction process might meet the requirements for feasibility.

Preliminary screening experiments were conducted to select suitable reagents. The results of these experiments indicated that at least three of the reagents tried would be effective for chromium removal under proper conditions of pH, etc. These were

(1) Aliquat 336, a quaternary amine salt, manufactured by General Mills. Its price was quoted at about $1 per pound.

(2) Alamine 336, a tertiary amine produced by the same company, said to be available at 80 cents per pound.

(3) Amberlite LA1, a secondary amine manufactured by Rohm and Haas, reported to cost 60 cents per pound.

Results obtained in preliminary experiments with these three reagents are summarized in Table 17.

In most of the subsequent work, Alamine 336 was employed. Aliquat 336 was not used because of a reported high solubility in water (1 percent). It is believed that Amberlite LA1 may have performed as well as Alamine 336, provided the pH was not allowed to exceed 2.0.

Undoubtedly there are a number of other reagents, probably all amines, which would be as suitable as those investigated.

Degree of Chromium Removal Obtainable. The batch experiments in Table 17 were all made on solutions containing 10 ppm of chromium. Additional batch experiments were made by the same procedures on more concentrated chromium solutions, using a 2.5 percent solution of Alamine 336 in a kerosene-isodecanol solvent. The results are shown in Table 18.

TABLE 18. BATCH EXTRACTION OF HEXAVALENT CHROMIUM FROM MORE CONCENTRATED SOLUTIONS USING ALAMINE 336

Expt. No.	Cr^{6} in Feed, ppm	Volume of Feed, ml	Volume of Extracting Solution, ml	Cr^{6} in Treated Solution, ppm	pH	Extraction, percent
100A	1000	400	200	27	1.5	97
58A	100	50	25	3	2.0	97
100B	27	100	25	1.5	1.8	93+

Indications from these experiments were that liquid-liquid extraction by Alamine should function efficiently over a wide range of chromium

TABLE 17. PERFORMANCE OF SEVERAL AMINES IN THE BATCH EXTRACTION OF HEXAVALENT CHROMIUM

Reagent	Chromium in Feed, ppm	Concentration of Reagent in Extracting Solution, percent	Volume Ratio Aqueous to Extracting Solution	Chromium in Treated Solution, ppm	pH Range	Extraction, percent
Aliquat 336	10	2.0	2:1	<0.2	0.3-8.0	98+
Aliquat 336	10	0.2	2:1	0.2-1.0	1-3.8	90-98
Aliquat 336	10	0.2	10:1	0.5-1.2	2	88-95
Alamine 336	10	2.0	2:1	0.2-0.8	0.3-1.0	92-98
Alamine 336	10	2.0	2:1	2.4-3.6	2.0-4.0	64-72
Alamine 336	10	0.2	2:1	0.4-1.1	1.0-1.5	89-96
Amberlite LA1	10	2.0	2:1	<2.0	0.3-2.0	98+
Amberlite LA1	10	0.2	2:1	0.9-1.3	0.3-1.5	87-91

concentration provided the pH of the solution was maintained at about 2 or lower and that there was sufficient reagent available for reaction with the chromium. Other investigators have obtained similar high extractions from solutions containing as much as 4000 ppm of hexavalent chromium.*

A number of continuous extraction experiments also were conducted in the mixer-settler unit shown in Figure 12. The results of these experiments are summarized in Table 19.

TABLE 19. EXTRACTION OF HEXAVALENT CHROMIUM IN CONTINUOUS OPERATIONS

Expt. No.	Cr^6 in Feed Solution, ppm	Cr^6 in Treated Solution, ppm	Chromium Extraction, percent	Remarks
52-1	14	0.05	99+	
53-1	10	0.10	99	
56-1	10	0.09	99+	
56-A	10	0.70	93	Lower extraction due to operation at pH 4
59-1	10	0.28	97	
61-1	10	0.04	99+	
62-1	10	1.3	89	Lower extraction due to excessive feed rate through mixer-settler
50-1	100	0.36	99+	
51-1	100	0.40	99+	

On the basis of these data, it was concluded that the requirement of reducing chromium to the required level of about 1 ppm or lower could be accomplished by liquid-liquid extraction.

Regeneration. The regenerability of Alamine 336 was investigated both in batch and continuous runs. In a typical batch run (Experiment 100A) 200 ml of a 2.5 percent solution of Alamine 336 in kerosene-isodecanol was partially loaded by extracting 400 ml of a chromic acid solution containing 1000 ppm of hexavalent chromium. After loading, the organic phase was stripped with 95 ml of 10 percent NaOH solution. The following tabulation shows the results obtained:

*"Chromium", General Mills Publication, Kankakee, Illinois (1961).

	Weight, g	Percent
Chromium in Feed Solution, 400 ml @ 1000 ppm Cr^6	0.400	100
Chromium Accounted for in Final Strip Solution, 95 ml @ 4400 ppm Cr^6	0.418	104

The stripped organic phase, in this experiment, was completely white and clear and contained at most only a few ppm of hexavalent chromium. This solution was reused once to extract an additional lot of chromic acid solution containing 1000 ppm of hexavalent chromium. The treated solution contained 35 ppm of hexavalent chromium. This compares with 27 ppm obtained in the first treatment.

The regenerability of "loaded" Alamine 336 solutions also was tested in the continuous mixer-settler runs. In one experiment the organic phase which had been collected separately was stripped with 4 percent sodium hydroxide by agitation for 15 minutes in the mixer-settler. Stripping was extremely rapid and, judging by the disappearance of the typical orange color in the organic phase, was completed within 5 minutes. The stripped solution then was employed in a subsequent run and yielded almost complete extraction of chromium.

On the basis of these data and considering the work of other investigators, there appeared to be little doubt that the Alamine reagent could be stripped and reused indefinitely. However, Alamine solutions loaded or even partially loaded with chromium, when allowed to stand overnight, lost the characteristic yellow-orange color and turned green. This was caused by the reduction of chromium, either by the kerosene or by the Alamine itself. Experiments with 2.5 percent solutions of Alamine 336 in solvents other than kerosene (mineral spirits and toluene) resulted in similar reduction. It is believed that the reduction is effected by the Alamine itself. If so, then an equivalent portion of the Alamine is in turn oxidized and may or may not still possess its full effectiveness.

Treatability of the Strip Solution. The regenerating solution, i.e., the sodium hydroxide solution that has been contacted with the "loaded" organic solution and now contains sodium chromate, should be sufficiently concentrated in chromium to minimize costs in further treatment. The laboratory work did not establish the maximum degree of concentration possible in a system in which dilute wastewaters (10-100 ppm of hexavalent chromium) are extracted and the organic phase is stripped with sodium hydroxide. On the basis of laboratory data, concentrations as great as 50:1 and possibly 100:1 should be readily obtainable. This is based on the fact that virtually complete extraction of chromium into the organic phase can be obtained at aqueous-organic ratios of 10:1, and on information from chemical producers that the organic phase can be stripped at aqueous-to-organic ratios of 1:5. In the case of stronger waste solutions, such as might be encountered in "save" rinse tanks or in countercurrent rinsing, similar concentration ratios might be achieved.

Oil content of the treated solutions. In all cases in the laboratory experiments, the treated solutions as produced either from the separatory funnel batch tests or the mixer-settler, carried off some of the organic phase. The amount of organic material in the treated solution was measured by total carbon analyses. Analytical data showed that the effluents, as produced, contained from about 150 to more than 400 ppm of carbon which corresponds to about 200 to 500 ppm of kerosene. In some instances there was a distinguishable layer of the organic fraction on the solution and in practically all other cases a thin, discontinuous iridescent film of oil was discernible.

Undoubtedly much of the contamination of the effluent by oil, or kerosene, was due to limitations of the laboratory mixer-settler which did not provide much settling area. It also was believed that the agitation employed in the mixer-settler operation was more violent than needed and that this contributed to the formation of more or less stable emulsions. In order to gain some idea of the amount of kerosene contributed by the inadequate settling area in the mixer-settler, the effluent samples were shaken and then permitted to settle for about 1 hour. A sample was then taken from the bottom of the sample container and analyzed for carbon. Typical results are shown in the following tabulation:

	Carbon Analysis, ppm	
Sample	As Produced	After Settling 1 Hour
50-1	400+	284
50-3	400+	320
50-6	168	144
51-1	148	94
51-2	112	55
51-4	400+	220
51-6	356	142
52-1	296	168
52-3	100	74
62-1	400+	128

These results, in general, indicated that a significant decrease in the carbon (i.e., kerosene) content was possible by providing additional settling time. The persistence of the carbon remaining after settling, however, should be regarded as a cautionary factor, which merits additional consideration.

This loss of carbonaceous material to the effluent may also indicate a serious loss of the extractant. For the purposes of the economic estimates which are presented later, it was assumed that reagent losses to the effluent will not exceed 10 ppm. An analysis for nitrogen (which is a distinctive component of the amine reagent) on one effluent solution indicates this loss may be several times as great as what has been allowed. Additional work on reagent loss is therefore believed to be very important.

Other Techniques Evaluated

Reduction of Chromium With Activated Carbon. During the experimentation on the adsorption of hexavalent chromium by activated carbon, it was noted that activated carbon reduced hexavalent chromium to the trivalent form under acidic conditions. In Experiment 14 (Table 15), for example, effluents were obtained which contained, on the average, 10 ppm trivalent chromium, indicating a reduction of 10 percent of the incoming chromium. The extent of reduction was affected primarily by pH and reduction could be eliminated by increasing the pH above 3.0. Although this effect was not studied in detail, one test was made to acquire some measure of the capacity of carbon for reducing hexavalent chromium. The results of this test indicated that 0.8 gram of chromium was reduced per gram of activated carbon added; however, the reaction did not appear to be completed. No additional study was made to determine the maximum amount of chromium which could be reduced per gram of activated carbon.

Reverse Osmosis for Chromium Removal. Considering the newness of the field of reverse osmosis, a brief study was made of this technique to determine its possible application to the treatment of metal-finishing wastes. Research on reverse osmosis has been primarily in the field of desalinization of brackish water; however, some effort has been devoted to the treatment of various industrial wastes.

The preliminary evaluation of reverse osmosis for chromium removal was conducted with a ROGA Model III Laboratory Reverse Osmosis Unit using chromic acid solutions containing about 100 ppm chromium. A total of eight reverse osmosis experiments on chromic acid solutions were made. Among the variables which were studied were the effects of pressure and feed concentration. The experimental results are given in Table 20.

TABLE 20. EXPERIMENTAL DATA ON CHROMIUM REMOVAL BY REVERSE OSMOSIS

Expt. No.	Pressure, psig	Flow, gph		Concentration, ppm Cr[a]		Indicated Percent Removal
		Concentrate	Permeate	Concentrate	Permeate	
1	500	17.6	1.8	104	44	58
2	350	19.0	1.3	104	45	57
3	200	--	--	104	46	56
4	200	13.6	0.8	83	35	58
				94	36	62
5	100	15.8	0.5	97	37	62
				70	39	44

TABLE 20. (Cont.)

Expt. No.	Pressure, psig	Flow, gph		Concentration, ppm Cr[a]		Indicated Percent Removal
		Concentrate	Permeate	Concentrate	Permeate	
6	500	23.8	1.6	76	54	29
				97	46	53
7[b]	500	--	--	34	9.5	72
				42	12.5	70
8[c]	500	--	--	112	40	64
				120	43	64
				140	49	65
				182	64	65

(a) Test solutions were prepared from chromic acid and deionized water.

(b) Mixed permeates from Experiments 4-6 were used as feed solution for this experiment.

(c) In this experiment, the concentrate stream was continuously fed back to the feed vessel during the run.

As shown in Table 20, percentage reductions of hexavalent chromium were only "fair", ranging from a low of 39 percent to a high of 72 percent. The results of these limited experiments suggest that reverse osmosis may have application as part of an overall wastewater treatment/recycle system for plating wastes, but considerably more experimental work would be required to confirm this.

Adsorption of Chromium on Activated Alumina. Because activated carbon was effective in adsorbing chromium from the waste solutions and because several other elements are reported to have been adsorbed on activated alumina, it was believed that this technique should be screened. In this assessment, powdered activated alumina with a particle size of 8 x 14 mesh was used. The procedure comprised mixing 10 grams of the alumina with 1 liter of solution containing 10 ppm chromium as dichromate and stirring the mixture for 30 minutes. The mixture then was filtered and the filtrate analyzed for hexavalent chromium content. The experimental results did not show any measurable chromium removal.

Preliminary Evaluation of Treatment Costs

In order to compare the various treatment processes studied during the initial phase of the program, an attempt was made to estimate the costs of the various techniques for removal of chromium. Although cost factors were not precise at this point in the program, and could change perhaps

significantly, depending on the outcome of future work, they were used, by necessity, as a primary basis for comparing the processes. The following sections discuss the procedures used in arriving at appropriate cost factors for each particular process.

Ion Flotation. The chemicals consumed in operating an ion flotation system were assumed to include the flotation collector solutions and any regenerating chemicals required if the collector was recovered. Air for flotation and associated supply costs were considered insignificant with respect to these materials.

Sufficient data were obtained in laboratory studies to determine the efficiency of certain collectors for removing chromium. Based on these data, the costs of flotation collectors for hexavalent chromium or trivalent chromium were calculated for solutions containing 10 ppm and 100 ppm chromium. The results of these calculations are summarized in Table 21. Also included are the collector costs for 100 ppm hexavalent chromium with the provision for regeneration and recovery of the collector which was studied very briefly.

TABLE 21. EFFICIENCY AND COSTS OF ION FLOTATION COLLECTORS FOR CHROMIUM REMOVAL

	Removal Attained[a], percent	Collector Requirement[a], lb/lb Cr	Costs[b]	
			$/lb Cr	$/1000 gal
Hexavalent Chromium:				
@ 100 ppm	91	5.0	1.65	1.32
@ 10 ppm	78	8.0	2.64	0.21
@ 100 ppm, with regeneration	90	1.3	0.43	0.34
Trivalent Chromium:				
@ 100 ppm	95	0.07	0.01	0.01
@ 10 ppm	94	0.70	0.14	0.01

(a) Based on experimental data shown in Figures 5 and 6 and in Tables 10 and 13.

(b) Based on mixed primary amine collectors @ $0.33/lb for hexavalent chromium and fatty acid collectors @ $0.20/lb for trivalent chromium.

The data in Table 21 indicate a 90 percent removal of hexavalent chromium at 100 ppm for $1.65 per pound of chromium. With regeneration and recovery of the collector, this is reduced to about $0.55 per pound of chromium including the added cost of regenerating chemicals, which would amount to an additional 20 to 30 percent over the values shown in Table 21. These results are based on limited small-scale experiments. Thus, if more effective reagent recovery could be obtained in larger scale equipment, a considerable further reduction in reagent cost could be realized.

For the removal of trivalent chromium, by contrast, the cost of the collector ranges from $0.01 to $0.14 per pound of chromium depending on the concentration. This cost would be relatively insignificant with respect to the cost of other reagents required, such as reductants for hexavalent chromium and caustic for precipitation of trivalent chromium. These latter chemicals are the same as those required in conventional treatment, thus the costs of the two processes would be similar.

None of these estimates take into account the cost of solvent if the flotation collectors are added in alcoholic solution. No estimate could be determined on this factor on the basis of the small-scale experiments. Whether or not a solvent is needed and the required concentration must be determined in larger scale equipment.

On the basis of a typical plant having a waste flow of 15 gallons per minute containing 100 ppm of chromium, it was assumed that the flotation process could be conducted with limited equipment comprising a 500-gallon flotation cell, a pump, and a small reagent feeder. An agitated tank and filter also would be needed for the regeneration and recovery of the spent flotation collector. It was estimated that the installed cost of this equipment would be about $4,500.

Adsorption on Activated Carbon. In evaluating the economic feasibility of an activated carbon process for the removal of chromium from waste plating rinse waters, several factors must be considered. These factors include such items as material costs, equipment costs, labor costs, whether materials can be regenerated for reuse, and whether any valuable contaminants, such as chromium, could be recovered.

Pittsburgh Type OL granular activated carbon is quite expensive compared with various other types of carbon available. The manufacturer's f.o.b. price is 39 cents per pound in lots of over 30,000 pounds. Other brands of activated carbons with approximately the same relative activity are available at about 50 percent less cost. It is possible that some of these less expensive materials also could effect high chromium removal.

Estimated costs were calculated for chromium removal by activated carbon and for the regeneration of the carbon, based on the bench-scale

experimental work with Pittsburgh Type OL granular activated carbon. The results are shown in Table 22. These data show the costs involved in two separate methods of carbon regeneration. The first method involves the use of sodium hydroxide to remove the chromium from the carbon as hexavalent chromium and a sulfuric acid wash to control the pH value of the carbon. The sodium hydroxide solution containing high concentrations of hexavalent chromium (as high as 30 grams per liter) then is either recovered or destroyed by conventional methods. Destruction would involve the treatment of relatively small volumes of the concentrated solution with sodium bisulfite to produce a chromium hydroxide sludge that could be hauled to dumps. As can be seen the material costs for this method would amount to about 39 cents per pound of chromium contained in the feed solution.

TABLE 22. ESTIMATED REAGENT COSTS FOR ACTIVATED CARBON REGENERATION AFTER ADSORPTION OF CHROMIUM

Reagents	Amount of Reagent Required, lb/lb Cr	Estimated Reagent Cost, $/lb Cr
Method I (sodium hydroxide)		
Regeneration:		
NaOH (sodium hydroxide) @ 3¢/lb	1.5	0.05
H_2SO_4 (sulfuric acid) @ 2¢/lb	2.0	0.04
Total cost of reagents for regeneration/lb Cr		0.09
Conventional Treatment:		
$Na_2S_2O_5$ (sodium bisulfite) @ 7¢/lb	2.8	0.20
H_2SO_4 @ 2¢/lb	1.4	0.03
NaOH @ 3¢/lb	2.3	0.07
Total cost of conventional treatment/lb Cr		0.30
Total cost of Method I, per lb Cr		0.39
Method II (sulfuric acid)		
Regeneration:		
H_2SO_4 @ 2¢/lb	3.0	0.06
Activated carbon @ 39¢/lb	0.2	0.08
Total cost for regeneration/lb Cr		0.14
Treatment:		
NaOH @ 3¢/lb	2.3	0.07
Total cost of Method II, per lb Cr		0.21

The second method of carbon regeneration involves the use of sulfuric acid to remove the chromium from the carbon as reduced chromium. With this method, some of the carbon would be consumed since it is believed that the reduction is carried out according to the following equation.

$$2H_2Cr_2O_7 + 6H_2SO_4 + 3C \rightarrow 2Cr_2(SO_4)_3 + 3CO_2 + 8H_2O.$$

In this reaction about 0.2 pound of carbon would be used per pound of chromium reduced. The highly concentrated acid solution could then be treated with sodium hydroxide to neutralize and precipitate a chromium hydroxide sludge. The cost of regeneration by this method, including carbon costs, would amount to about 21 cents per pound of chromium fed to the process in the waste effluent.

On the basis of the "average" waste flow conditions cited previously (15 gallons per minute at 100 ppm of chromium) and an 8-hour operating day, it was estimated that a 21 cubic foot carbon column would be required for the process. This size would permit regenerations at intervals of about one week. If hexavalent chromium is destroyed and not recovered, a 250-gallon agitated tank also would be needed for this purpose.

Equipment for this process was estimated at about $5,500.

Liquid-Liquid Extraction. Although there are a number of uncertainties concerning the precise type and size of equipment, optimum operating conditions, etc., required for the liquid-liquid extraction treatment of metal-finishing wastes, enough information was obtained in the laboratory campaign to project preliminary capital and operating costs. Figure 14 is a flowsheet of the speculative process for which the estimates were made.

Capital costs were arrived at by estimating the installed cost of equipment that would be necessary to treat 15 gallons per minute of waste rinse water containing from 1 to 100 ppm of hexavalent chromium.

Installed costs of the equipment including the necessary pumps, piping, etc., were estimated to be about $8400.

A major factor in operating cost is the quantity of chromium that must be treated. The operating cost estimates were made therefore for levels of chromium concentration: 10, 30, and 100 ppm at a flow rate of 15 gallons per minute. Details of these estimates are shown in Table 23.

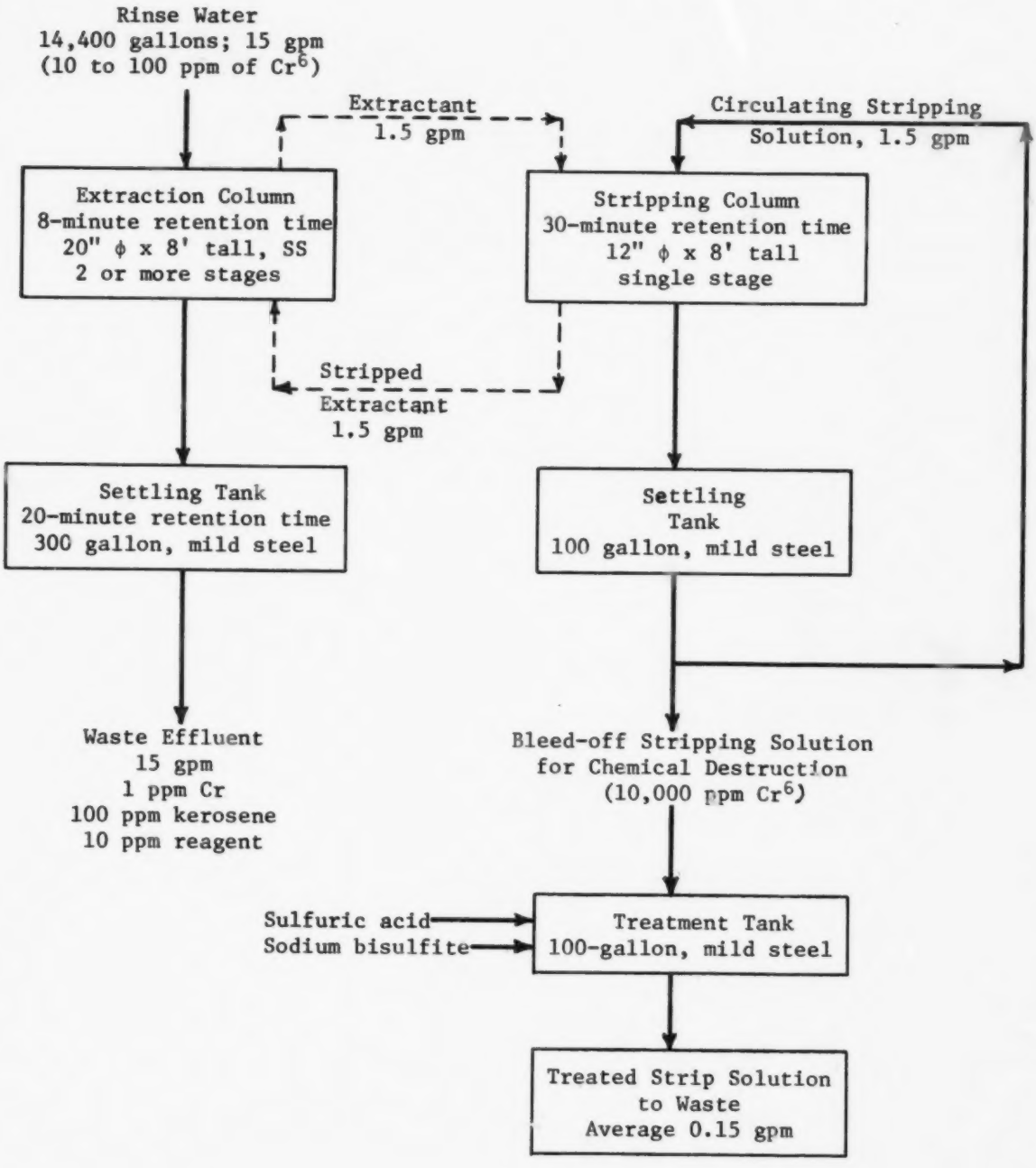


FIGURE 14. FLOWSHEET ASSUMED FOR COST ESTIMATES

TABLE 23. ECONOMIC FACTORS IN OPERATING COSTS[a] FOR LIQUID-LIQUID EXTRACTION

lb Chromium/Day in Effluent:		1.2			3.6			12.0		
Chromium, ppm:		10			30			100		
	Unit Cost, $	lb	Cost, $	Cost/hr, $	lb	Cost, $	Cost/hr, $	lb	Cost, $	Cost/hr, $
Sodium hydroxide	0.03/lb	5	0.15		15	0.45		50	1.50	
Kerosene	0.16/gal.	2	0.32		2	0.32		2	0.32	
Reagent	0.60/lb	1.2	0.96		1.2	0.96		1.2	0.96	
Sulfuric acid	0.02/lb	7	0.14		20	0.40		65	1.30	
Sodium bisulfite	0.07/lb	3.4	0.24		10	0.70		34	2.40	
Labor[b]	3.00/hr	0.2	0.60		0.5	1.50		1.0	3.00	
Power	0.03/kwhr	20	0.60		20	0.60		20	0.60	
Total			3.01	0.19		4.93	0.31		10.08	0.67

(a) All costs based on 16-hour day.

(b) Labor cost calculated by assuming that practically all labor is used in treating stripped solution at 1 hour per batch treatment. At 10 ppm treatment estimated to be every 5 days; at 30 ppm every other day; at 100 ppm, daily.

Liquid-liquid extraction would afford a good opportunity for chromium recovery, because it could produce a strip solution containing at least 10 and possibly up to 20 grams per liter of hexavalent chromium. Provided enough chromium is involved, significant credit might be realized from the recovery of chromium.

Provided the treated effluent did not contain undesirably high concentrations of oil, at least some of it might be reusable in rinsing. The attendant savings in water and sewerage costs would constitute a credit for the operation.

Comparison of Experimental and Conventional Processes. In addition to the above cost estimates for the experimental processes, two conventional techniques also were evaluated for comparative purposes. The conventional methods selected were ion exchange and conventional reduction with sodium bisulfite.

Estimates of the operating and equipment costs for each of these methods was made using the same basis as mentioned previously (15 gallons per minute at 100 ppm chromium). A comparison of these costs with those determined for the experimental techniques is shown in Table 24.

TABLE 24. PRELIMINARY COMPARISON OF COSTS FOR SELECTED EXPERIMENTAL AND CONVENTIONAL TREATMENT METHODS

	Reagent Cost, $/lb Cr	Capital Cost[a], $	Operating Cost[b], $/day
Removal Only:			
Conventional Method with $Na_2S_2O_5$	0.30	8,000	10.00
Ion Exchange	0.58	8,500	12.50
Carbon Adsorption	0.21	5,500	8.00
Liquid-Liquid Extraction	0.54	8,500	11.00
Ion Flotation	0.55	4,500	10.50
Removal Plus Recovery of Chromium:			
Ion Exchange	0.29	10,000	7.50[c]
Carbon Adsorption	0.16	7,000	5.50[c]

(a) Based on waste flow rate of 15 gallons per minute and contaminant level up to 100 ppm.
(b) Based on 8-hour day, 250 days/year; waste flow rate of 15 gallons per minute, and contaminant level of 100 ppm. Includes cost of reagents, labor, power, fuel, maintenance at 5 percent per year, and depreciation at 13 percent per year.
(c) Includes in addition to the items listed in (b) a credit for recovery based on chromium at $0.65/lb.

This economic comparison indicated that the carbon adsorption process for chromium removal may have economic advantage over the other methods listed. Carbon adsorption also appeared competitive with ion exchange when recovery of chromium is considered; however, the possible saving in rinse water by these methods was not included.

Phase 2: Demonstration Plant Study

The activated carbon adsorption technique was selected for further development on a pilot-plant scale for the following reasons:

(1) Apparent economic advantage over conventional waste treatment processes within the range of rinsewater flow rates and chromium concentrations normally encountered in small plating plants

(2) Operational simplicity

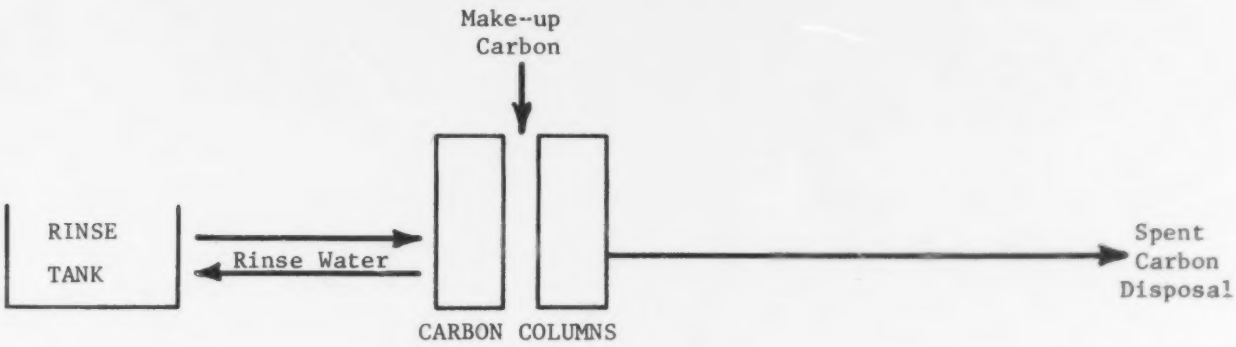
(3) Low floor-space requirements.

A preliminary evaluation of the process on the basis of Phase 1 results indicated that three basic techniques or process modifications employing activated carbon adsorption might be developed for use by the small plater. These process modifications are illustrated in Figure 15.

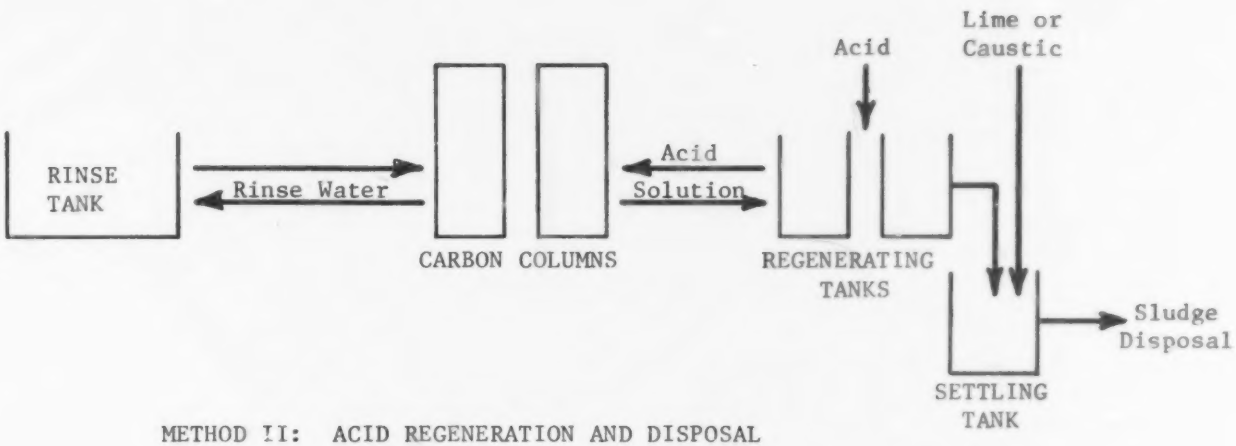
The first method constitutes the use of carbon as a single adsorption material followed by disposal of the loaded carbon as a solid waste. During the adsorption cycle, the chromium rinse water is recirculated from the rinse tank, through the carbon columns, and then reused for rinsing. This permits the attainment of high carbon loading capacities, since the chromium content of the water can be allowed to increase to the point where it impairs rinsing efficiency. The ultimate adsorption capacities for this method of operation were determined experimentally in previous laboratory studies.

The second and third methods of operation also may be conducted as described above, except that the loaded carbon is regenerated chemically after each adsorption cycle and reused for subsequent cycles. Various methods for regeneration were investigated in detail during both laboratory work and pilot-plant operations. In Method II, regeneration is carried out by recirculating dilute sulfuric acid through the carbon bed. Chromium is reduced during this treatment, and with a subsequent caustic addition to the effluent, is precipitated as trivalent chromium hydroxide which can be removed by sedimentation. Chromium ultimately ends up as a sludge which would be disposed of as a solid waste material.

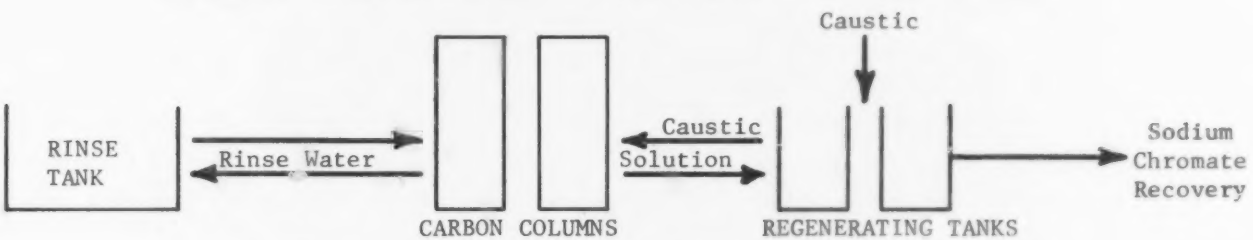
With caustic regeneration, as shown in Method III, chromium is removed from the carbon as hexavalent chromium, possibly suitable for recovery and reuse within the plant. The spent regenerating solution contains primarily sodium chromate with small amounts of excess caustic. It might be reusable in post-treatment solutions for zinc and cadmium plating



METHOD I: SINGLE ADSORPTION AND DISPOSAL



METHOD II: ACID REGENERATION AND DISPOSAL



METHOD III: CAUSTIC REGENERATION AND RECOVERY

FIGURE 15. ALTERNATIVE PROCESSES FOR CHROMIUM REMOVAL BY ACTIVATED CARBON

operations or converted to chromic acid in a single, small ion exchange unit. Regeneration with caustic, however, reclaimed only about 2/3 of the chromium in previous laboratory studies, and ultimately the remaining chromium must be removed by acid regeneration or the spent carbon disposed of as in Method I.

Pilot-Scale Investigation

Equipment and Procedure. The second phase of experimental work on activated carbon was conducted in pilot-plant equipment employing carbon columns of 1-foot-ID by 6 feet in length. The pilot-plant system was installed at a plating plant in Columbus, Ohio, and operated on actual chromium rinse waters produced by this company. These rinse waters contained generally between 100 and 820 ppm hexavalent chromium at pH values ranging from 2.0 to 3.0. The water was used directly as feed to the carbon columns with no prior treatment or pH adjustment.

Pilot-plant equipment was installed as shown in Figure 16. Basically, the system consisted of two 1000-gallon rubber-lined tanks, an adsorption module containing two carbon columns, and associated pumps, piping, and instruments to operate the system. The adsorption module was a standard ion exchange package unit purchased from Illinois Water Treatment Company but charged with activated carbon beds instead of ion exchange resins. Each column was filled with 100 pounds of Pittsburgh Type OL activated carbon. The unit also was modified by installing additional piping and valves to permit recirculation of the regenerating solutions. Piping was arranged so that one column could be regenerated while the other column was undergoing adsorption.

In operating the system, rinse water was pumped at about 5 gpm into one or both of the holding tanks. The water was then recirculated in these tanks to equalize concentrations and pumped to the adsorption unit. Effluent water from the carbon columns was sampled periodically and discarded to the sewer. Samples of the feed also were obtained periodically. These samples were analyzed to determine pH and chromium concentration. Adsorption was continued until a "breakthrough" was achieved, e.g., effluent samples reached about 10 ppm in hexavalent chromium concentration.

Following adsorption, the loaded carbon columns were regenerated by one of two techniques, e.g., either dilute sulfuric acid or caustic solution was recirculated through the appropriate column. Normally, regeneration was carried out at flow rates of 1 to 2 gpm and for various periods up to 16 continuous hours. The regenerating solution was then pumped from the column and analyzed to determine the amount of chromium stripped. Extensive washing of the column with water also was employed to complete a material balance on chromium. Analyses for chromium were conducted according to the procedures outlined in Appendix B.

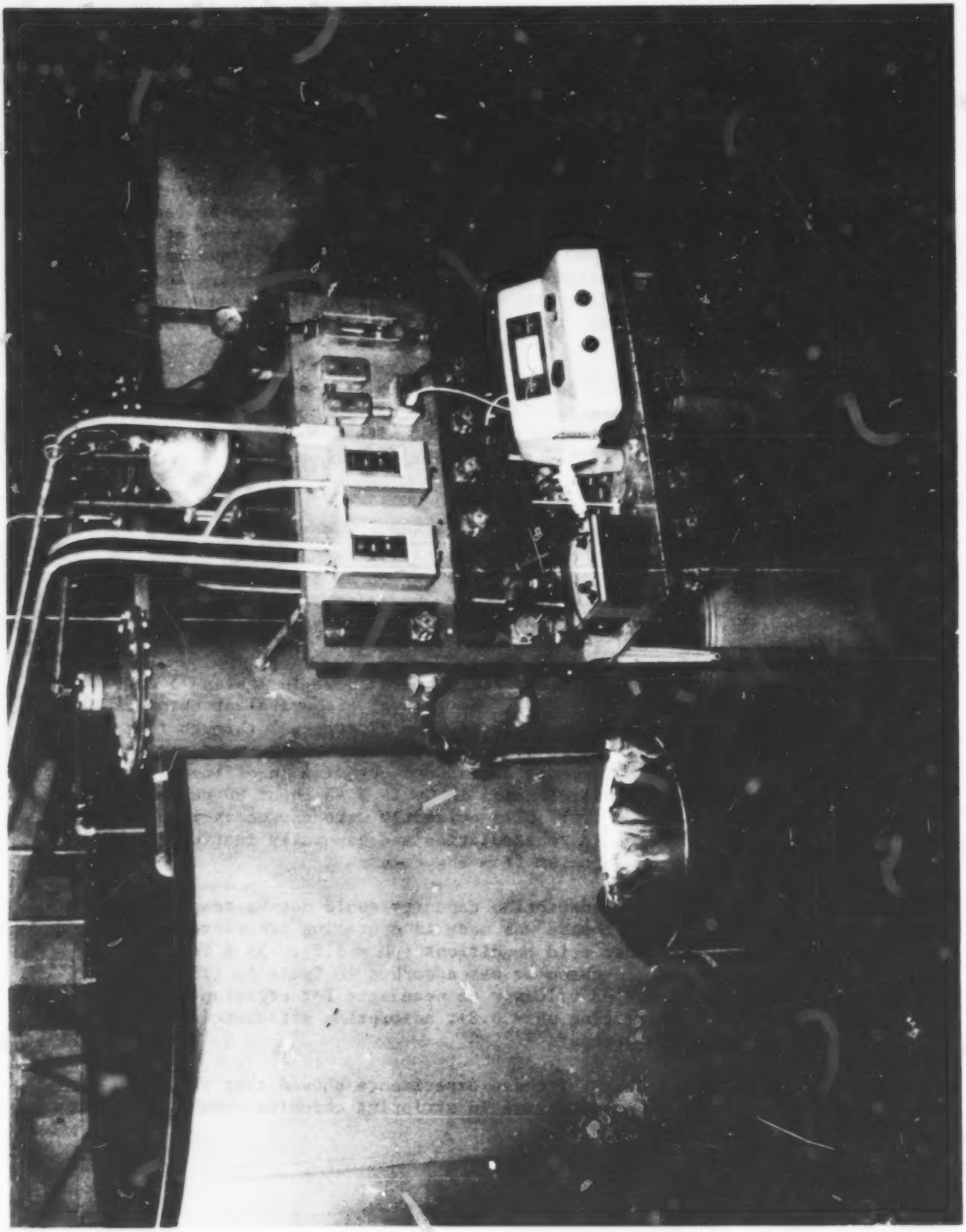


FIGURE 16. PILOT-PLANT CARBON ADSORPTION SYSTEM

The initial experiment in the pilot-plant system consisted of a preliminary operation to check out the system and to develop operating procedures for subsequent detailed runs. Column No. 1 was used for this preliminary run and was charged with 50 pounds of Pittsburgh Type OL activated carbon. Prior to feeding, the carbon was acid washed by recirculating a 5 percent sulfuric acid solution through it for several hours. This acid wash procedure was found necessary from laboratory work to remove basic materials from the carbon and to lower the column pH to a level conducive to high adsorption of hexavalent chromium. Following the acid wash treatment, the column was operated by feeding rinse water containing 352 ppm of hexavalent chromium at a pH of 2.3 and at flow rates of 1 to 2 gpm. A total of 471 gallons of rinse water from the plating plant was treated during the initial experiment. Analyses of the effluent samples indicated that essentially 100 percent of the chromium was removed except for the final 40 gallons when the chromium content of the effluent rose to about 1.0 ppm.

Following the preliminary operation, a series of continuous adsorption and regeneration runs were made employing both carbon columns of the system. Each column was completely filled with carbon (100 pounds) and acid washed with sulfuric acid prior to beginning each adsorption cycle.

Results of Sulfuric Acid Regeneration Method. Initial experiments were concerned primarily with the acid regeneration technique in which the adsorbed chromium was stripped from the carbon as trivalent chromium sulfate with dilute sulfuric acid. The operation included a total of 6 adsorption cycles and 5 regeneration cycles under various operating conditions.

The pertinent data from these experiments are shown in Tables 25 and 26. During adsorption runs (Table 25), the removal of hexavalent chromium from the rinse water was high (greater than 99 percent) through four cycles of operation. In Cycle 3, however, somewhat poorer operation was obtained because of the presence of reduced chromium in effluent samples. This lowered adsorption efficiencies in Cycle 3 to about 90 percent for total chromium. The poorer results evidently were caused by insufficient time being allowed for acid recirculation and generally ineffective washing of the reduced chromium from the column.

In Cycle 5, the very low adsorption capacity could not be compared with other results because a change was made in operating procedure to evaluate adsorption under less acid conditions (pH = 6.0). As a result of this change, very little chromium was adsorbed in Cycle 5. This run demonstrated that lower pH values were necessary for efficient adsorption. In Cycle 5a (starting pH = 3.8), adsorption efficiencies again increased to about 95 percent.

Significantly, the results of these experiments showed that acid regeneration was not completely effective in stripping chromium once it had been

TABLE 25. PILOT-PLANT ADSORPTION DATA ON COLUMN NO. 1, ACID REGENERATION

	Duration of Run		Feed Data			Effluent Data					Calculated Chromium Adsorbed			Apparent Carbon Loading Capacity
	Operating days	Feeding hours	Total gal.	pH	ppm Cr^{+6}	Start pH	Final pH	Typical ppm Cr^{+6}	Final ppm Cr^{+6}	Typical ppm Cr^{+3}	Percent Cr^{+6}	Percent Total Cr	lb	lb Cr/lb Carbon
Cycle 1	5	28	2766	2.3-2.6	250-460	1.6	8.6	<0.05	9.7	--	>99	>99	9.45	0.095
Cycle 2	4	15	1950	1.9-2.0	410-820	1.1	5.4	0.1	1.0	5.5	>99	>99	10.11	0.147
Cycle 3	2	10	950	2.0	725-750	2.1	4.7	3	5.4	75	>99	90	5.34	0.126
Cycle 4	3	15	1380	2.1-2.4	275-375	2.0	4.7	<0.05	6.1	30	>99	90	3.80	0.094
Cycle 5	1	4	374	2.4	250	6.0	6.0	130	195	--	50	50	0.40	0.077
Cycle 5a	3	28	2978	2.2-3.1	100-260	3.8	6.5	<0.05	41	1.3	95	95	3.57	0.105

TABLE 26. PILOT-PLANT REGENERATION DATA ON COLUMN NO. 1

	Regenerating Solutions			Wash Water	Chromium Concentrations		Chromium Stripped From Carbon		
	lb H_2SO_4	gal H_2O	Percent H_2SO_4	gal	ppm Cr^{+6}	ppm Cr^{+3}	lb Cr^{+6}	lb Cr^{+3}	lb Total Cr
Cycle 1	42	30	3-21	80	0	1,000-18,300	0	4.87	4.87
Cycle 2	24	45	6	100	1200-4100	500-20,000	0.51	6.88	7.39
Cycle 3	44	90	3-6	120	0	14-12,000	0	7.00	7.00
Cycle 4	24	45	6	105	72	2,600-6,200	0.10	2.05	2.15
Cycle 5	6(a)	15	5	35	1800	--	0.75	--	0.75

(a) In this run, 10 pounds of caustic was used prior to treatment with acid.

adsorbed by the carbon. This is illustrated in Figure 17 which compares adsorption and regeneration data for each run. Overall, only 76 percent of the adsorbed chromium was removed through 5 cycles of acid regeneration.

Results of Caustic Regeneration Method. Considerably more data were obtained on the second method of operation involving regeneration with caustic to remove hexavalent chromium followed by an acid wash treatment to remove residual caustic and condition the column for subsequent adsorption cycles. Operating data and results through 10 cycles of adsorption and caustic regeneration are shown in Tables 27 and 28.

The adsorption data in Table 27 indicate generally that chromium adsorption capacities were somewhat better with caustic regeneration than with acid regeneration. The weight of chromium adsorbed per cycle remained fairly constant at about 5.0 pounds through 7 cycles of operation neglecting the initial run which was low because of insufficient acid washing of the carbon prior to undertaking this series of experiments. Adsorption efficiency ranged from about 90 to over 99 percent through all runs. The lower efficiencies were traced to the presence of trivalent chromium in effluent samples. This probably was caused by insufficient washing of the column leaving residual trivalent chromium or to the formation of trivalent chromium during adsorption by employing high chromium concentrations in the feed.

Adsorption capacities in two of the final runs (Cycles 8 and 9) decreased to about 3.0 pounds for unexplained reasons. It was suspected, however, that the poorer adsorption was the result of a gradual buildup of chromium on the carbon which was not removed by regeneration. This is illustrated in Figure 18. As was found in previous runs, caustic regeneration also was not completely effective in stripping chromium from the carbon. Overall only 76 percent of the adsorbed chromium was removed through 10 cycles of operation. In only two runs was the amount of chromium stripped equal to or greater than the amount adsorbed in the same cycle.

Discussion of Pilot-Plant Runs. The results of the pilot-plant study demonstrated that actual chromium rinse waters can be effectively treated with activated carbon but also that important areas exist for additional study or refinement of the process. One area which needs additional study is in the apparent loss of adsorptive capacity after multiple cycles of operation with either caustic or acid regeneration. In the caustic regeneration runs, for example, there was indication that after 8 and 9 cycles, serious loss of adsorptive capacity occurred. However, in Cycle 10, there was a partial recovery in the system with adsorptive capacities of 4 pounds of chromium per 100 pounds of carbon again being achieved. The reasons for the improved results were not fully determined but were believed due to more effective regeneration procedures employed in the preceding cycle. Not enough cycles were conducted during the campaign to fully evaluate at

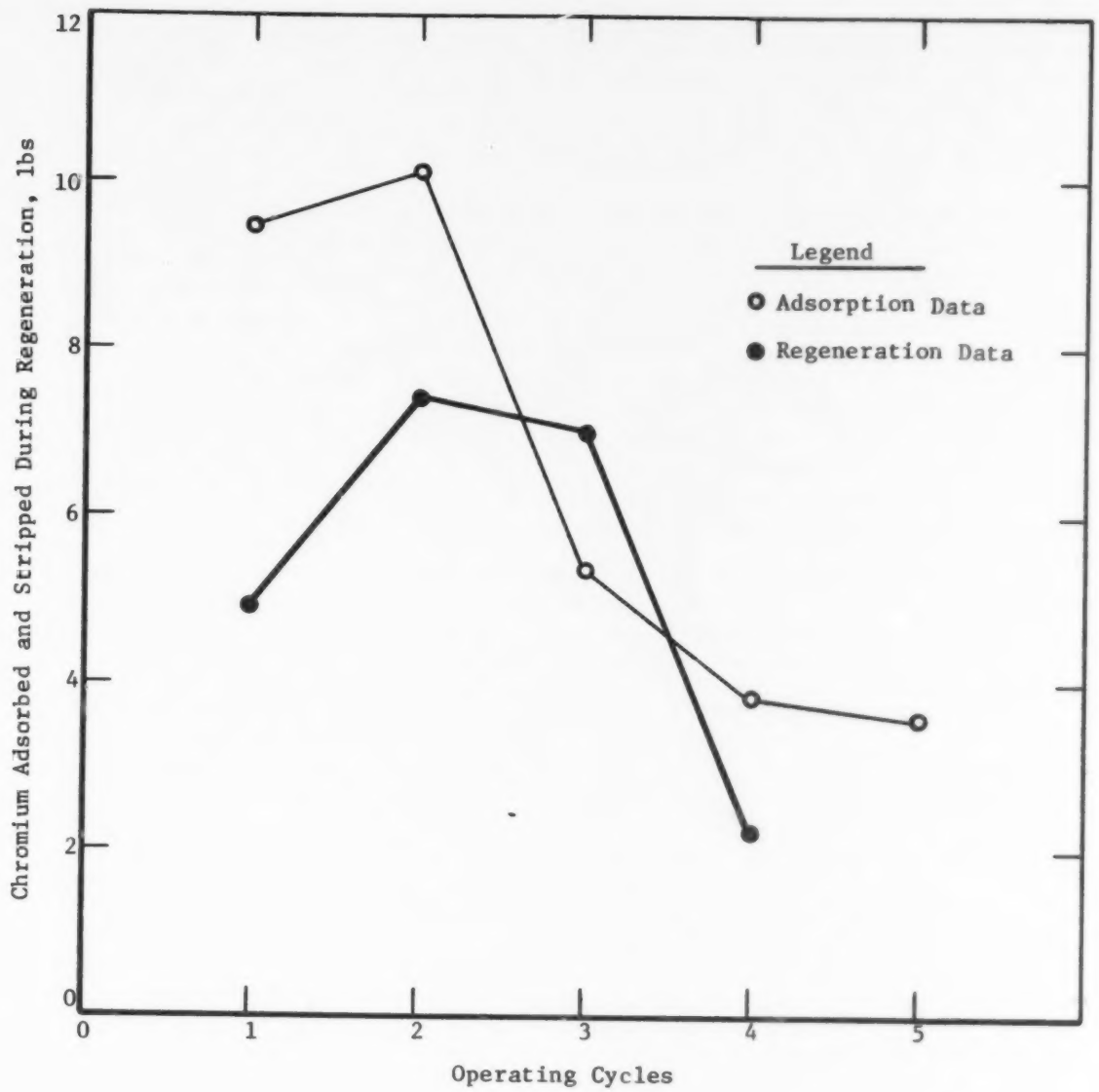


FIGURE 17. PILOT-PLANT DATA ON ADSORPTION AND ACID REGENERATION

TABLE 27. PILOT-PLANT ADSORPTION DATA ON COLUMN NO. 2, CAUSTIC REGENERATION

	Duration of Run		Feed Data			Effluent Data					Calculated Chromium Adsorbed			Apparent Carbon Loading Capacity(a)
	Operating days	Feeding hours	Total gal.	pH	ppm Cr^{+6}	Start pH	Final pH	Typical ppm Cr^{+6}	Final ppm Cr^{+6}	Typical ppm Cr^{+3}	Percent Cr^{+6}	Percent Total Cr	lb	lb Cr/lb Carbon
Cycle 1	2	10	1123	2.2	310	1.2	9.3	<0.05	10	—	>99	>99	2.91	0.029
Cycle 2	4	32	3860	2.6-3.0	110-240	2.0	7.3	<0.05	1.6	--	>99	>99	5.07	0.067
Cycle 3	4	23	2055	2.0-2.2	320-725	2.5	6.9	<0.05	3.5	0.8	>99	>99	7.51	0.110
Cycle 4	2	11	1204	2.0-2.2	500-560	1.5	5.0	1	2.5	28	>99	95	4.96	0.116
Cycle 5	1	11	1260	2.2	400-600	2.3	5.1	1	6.6	60	>99	90	4.72	0.112
Cycle 6	3	21	2457	2.5	190-343	2.7	6.3	0.1	9.4	3	>99	98	5.40	0.128
Cycle 7	3	23	2535	2.3-2.6	176-346	2.8	5.3	1	63	4	>99	97	5.22	0.155
Cycle 8	2	14	1557	2.4	142-441	2.5	3.7	0.3	102	25	>99	90	3.31	0.157
Cycle 9	1	8	927	2.2	340	3.3	4.6	1	38	16	>99	95	2.49	0.155
Cycle 10	2	16	1933	2.2-2.6	171-351	2.1	4.8	<0.05	25	10	>99	95	4.01	0.146

(a) Includes chromium not removed in preceding runs.

TABLE 28. PILOT-PLANT REGENERATION DATA ON COLUMN NO. 2

	Regenerating Solution		Acid Wash		Wash Water	Chromium Concentrations		Chromium Stripped From Carbon		
	lb NaOH	gal. H_2O	lb H_2SO_4	gal. H_2O	gal.	ppm Cr^{+6}	ppm Cr^{+3}	lb Cr^{+6}	lb Cr^{+3}	lb Total Cr
Cycle 1	5	15	9	15	55	3,800	240-3000	0.58	0.70	1.28
Cycle 2	14	30	16	15	70	480-10,200	3,800	1.63	1.63	3.26
Cycle 3	15	15	16	15	35	18,000	1,600	3.53	0.81	4.34
Cycle 4	15	15	16	15	70	8,500-19,000	3600-5800	3.55	1.50	5.05
Cycle 5	13	15	12	15	120	8,100-13,700	21-2400	3.38	0.50	3.88
Cycle 6	12	15	12	15	70	4,800-11,700	970	2.02	0.43	2.45
Cycle 7	14	15	20	30	200	5,600-16,800	1,800	2.69	0.46	3.15
Cycle 8	20	15	16	15	75	1,700-16,400	200-1000	2.47	0.25	2.72
Cycle 9	25	15	44	30	150	80-1,800	160-11,700	0.35	4.48	4.83
Cycle 10	25	15	20	15	75	320-9,500	1000-5,400	2.35	1.35	3.70

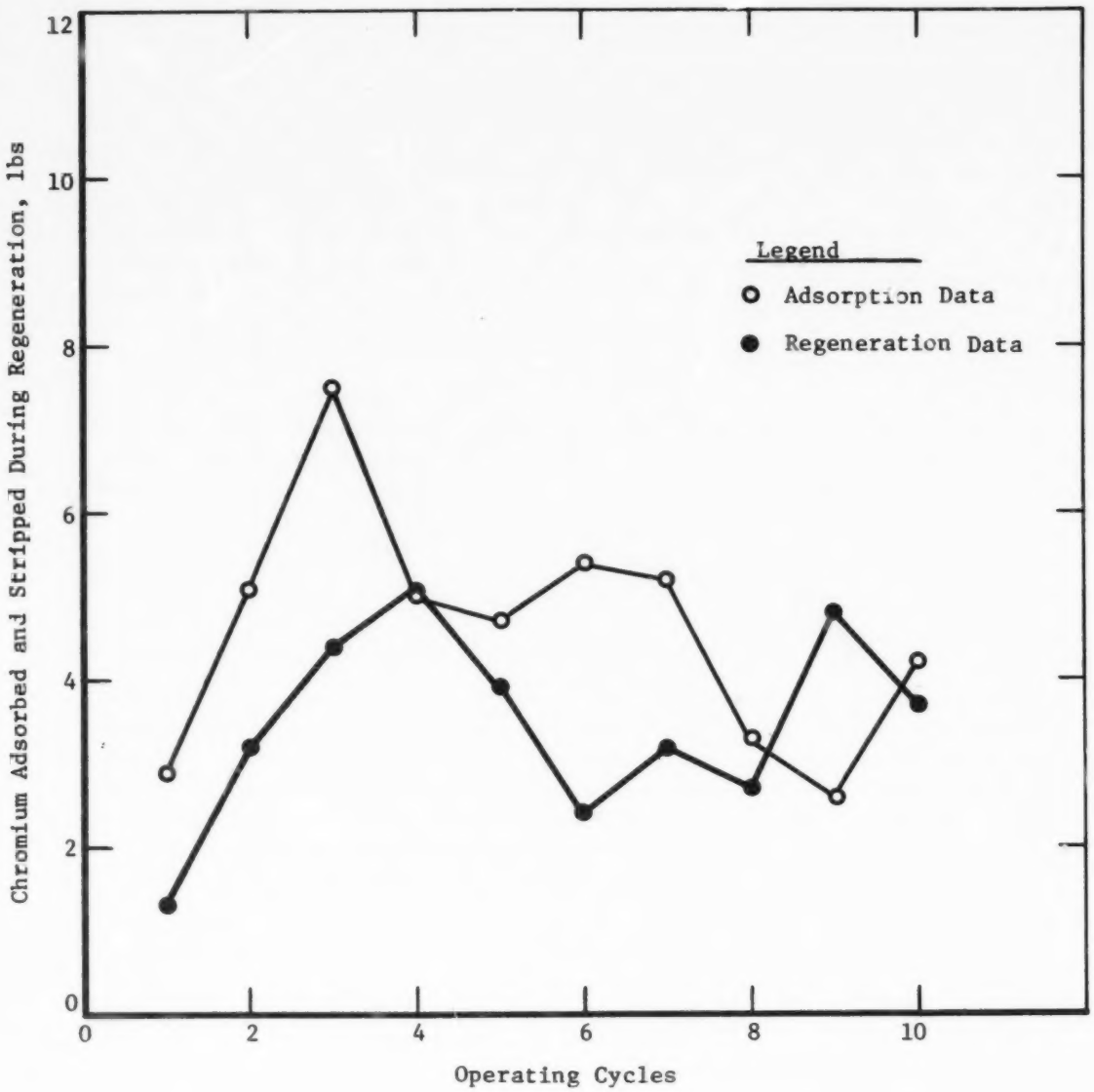


FIGURE 18. PILOT-PLANT DATA ON ADSORPTION AND CAUSTIC REGENERATION

what point the original carbon would become ineffective and need replacement. This also applies to the acid regeneration runs in which only 5 cycles were conducted and a much more serious loss of adsorptive capacity was noted.

In an effort to evaluate further the loss of adsorption efficiency experienced in pilot-plant runs, several confirmatory experiments also were conducted in the laboratory. In these experiments, series of adsorption and regeneration treatments were made on a 5-gram sample of activated carbon similar to that used in the pilot-plant runs. Both adsorption and regeneration cycles were conducted by magnetically stirring the samples in a beaker for periods up to 1 hour. The solution used in the adsorption cycles contained 1000 ppm hexavalent chromium. Solution pH was maintained at 3.0. These starting conditions were selected to achieve final equilibrium conditions closely approximating those obtained in the pilot-plant operation, e.g., 300-500 ppm Cr and 3.0 pH.

The results of these laboratory experiments are compared with the pilot-plant runs in Figures 19 and 20. Significantly, the laboratory data points could be approximated closely by the linear relationships shown in these figures. The pilot-plant data generally reflect a much greater variation between individual runs, but indicate the same trend after several cycles. Variations were explained as being due to changes in operating conditions such as feed concentration, pH, etc.

On the basis of the extrapolated linear relationship shown in these figures, it appears that adsorption capacities gradually decrease under either method of regeneration. Degradation of the carbon with acid is much greater than with caustic regeneration. For example, after 100 operating cycles, the predicted adsorption capacities are more than 0.03 pound per pound of carbon with caustic compared to less than 0.01 pound with acid regeneration. These data indicate a much shorter life of the carbon bed with acid treatment; however, replacement of the carbon probably would be required in either case. The optimum point at which carbon would be replaced cannot be established solely on the basis of the data presently available. Extrapolated data from these figures indicate that more than 100 cycles might be achieved with caustic treatment before replacing the bed. Actual experimental data, however, were obtained through only 10 cycles of operation. An extensive operating campaign would be needed to adequately extend the experimental data to a point where an accurate prediction of carbon life could be made.

Another aspect of the process which is not fully understood involves stripping of the adsorbed chromium from the carbon during the regeneration cycle. Incomplete stripping generally occurred during all runs with up to 10 percent chromium remaining on the carbon in several caustic regeneration runs. Even though this residual chromium was present, an additional 4 to 5 pounds of chromium could be adsorbed in the subsequent cycles. Whether or not adsorption capacities could be increased significantly if complete regeneration were achieved, remains to be established. The reasons for incomplete stripping were not investigated during this study; however, it could possibly be caused by operation with feeds

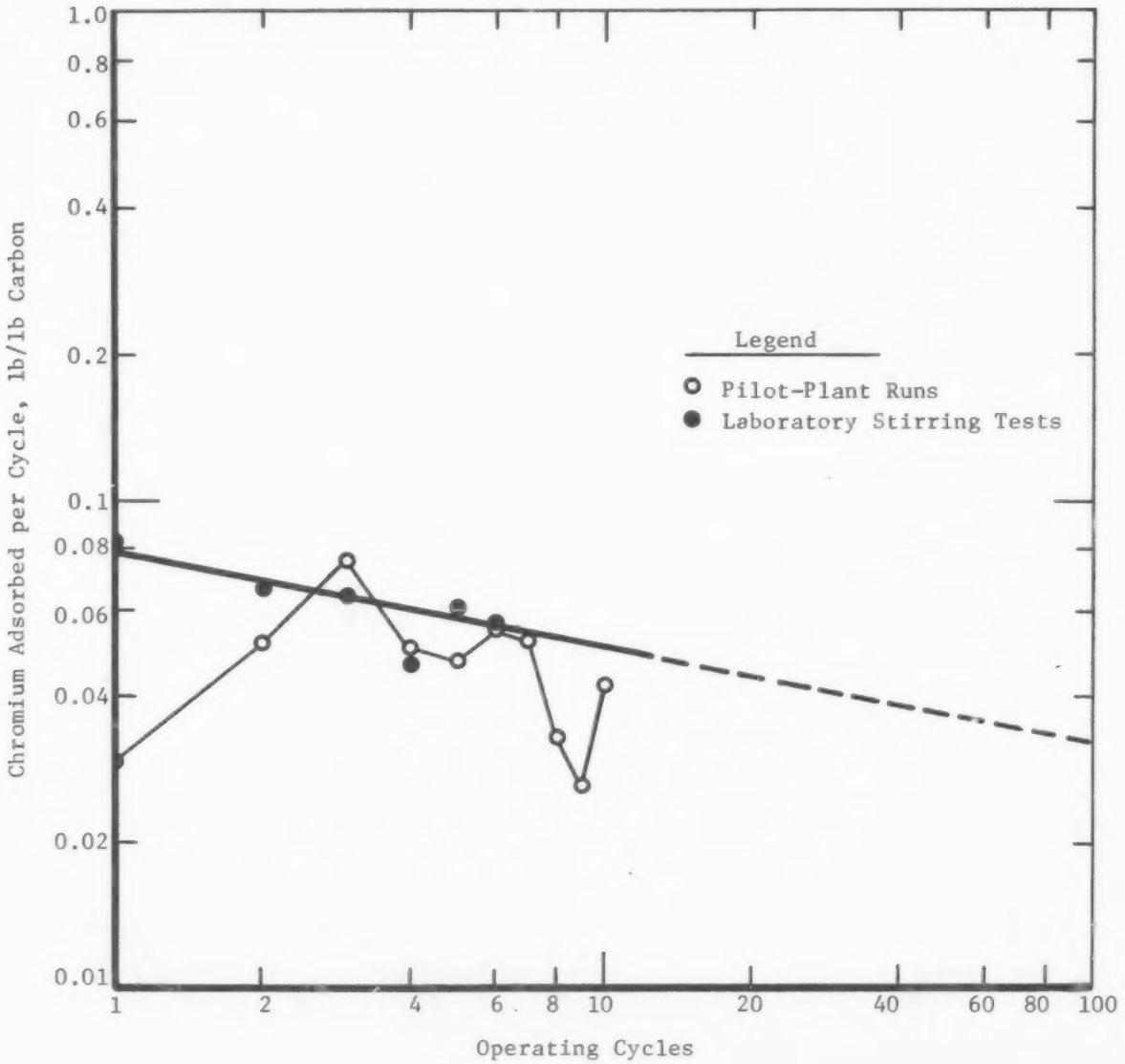


FIGURE 19. ADSORPTION CAPACITIES FOR HEXAVALENT CHROMIUM AFTER MULTIPLE CYCLES WITH INTERMEDIATE CAUSTIC REGENERATION

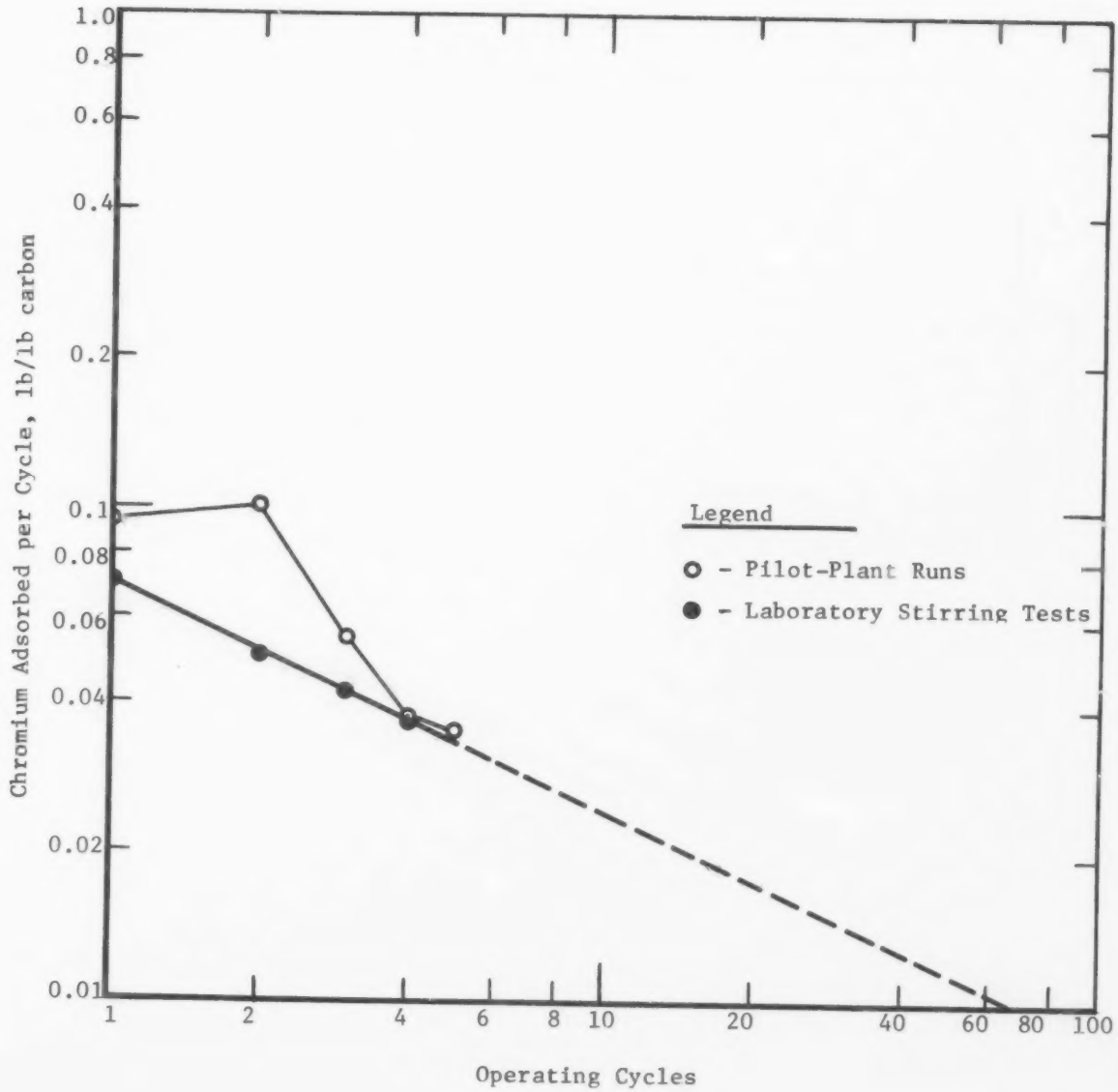


FIGURE 20. ADSORPTION CAPACITIES FOR HEXAVALENT CHROMIUM AFTER MULTIPLE CYCLES WITH INTERMEDIATE ACID REGENERATION

containing high chromium concentrations and at low pH values. Reduction of chromium during adsorption was found to occur at pH values below about 3.0. During reduction, chromium oxide (Cr_2O_3) probably was produced. This material, which is only partially soluble in dilute sulfuric acid, would be stripped very slowly during the regeneration cycle. Added evidence that this might occur was observed when complete stripping of the loaded carbon was obtained in boiling dilute sulfuric acid in laboratory experiments.

Feed rinse waters obtained during the pilot-plant study contained considerably higher concentrations of chromium than were originally anticipated. This also could have influenced reduction of chromium during adsorption and inability to completely strip the carbon. Use of other feed streams containing less than 100 ppm hexavalent chromium might have improved results.

Although some questions were not resolved during the campaign, sufficient data were obtained to demonstrate the technical feasibility of the process. Adsorption and removal of hexavalent chromium was greater than 99 percent in all but two runs. In these two runs, lower adsorption could be accounted for by changes in operating procedure. Removal of total chromium was somewhat poorer (90 to 99 percent) due to the presence of trivalent chromium observed during several runs. This probably was the result of insufficient washing of the carbon after regeneration or to the reduction of incoming chromium during adsorption. Operating performance generally was excellent during the entire pilot-plant study in which more than 29,000 gallons of rinse water and about 80 pounds of chromium were treated in the system. In many cases, the system was operated unattended with no problems being experienced. Operation in a continuous manner is therefore believed practical for commercial plating plant installations.

SECTION VI

ECONOMIC EVALUATION OF PROCESS

On the basis of pilot-scale and laboratory studies conducted in Phase 2, operating costs were reevaluated for the carbon adsorption process and compared with the conventional treatment method using sodium bisulfite. The results of Phase 2 indicated the necessity for carbon replacement at regular intervals which was not considered in the previous evaluation.

Calculations of chemical costs for the acid regeneration and the caustic regeneration processes were made assuming the linear relationships shown in Figures 19 and 20. The results for 20-cycle and 50-cycle replacement intervals are shown in Table 29 and compared with conventional treatment. Costs for other operating cycles are illustrated in Figure 21. It should be noted that unit costs of raw material (caustic and acid) were selected to represent closely the actual costs incurred by small plating shops in purchasing limited quantities of materials. These costs are significantly higher than used in the previous economic evaluation.

The data shown in Table 29 indicate that chemical costs for the acid regeneration process are about $0.91 and $0.73 per pound of chromium if 25 and 50 cycles of adsorption, respectively, can be achieved before carbon replacement. Above 50 operating cycles, the carbon replacement cost has very little effect on the overall economics (see Figure 21). On the same basis, the chemical costs for caustic regeneration are about $0.69 and $0.50 per pound of chromium removed for 20 and 50 cycles, respectively. This cost, however, does not include any credits for recovery of sodium chromate.

In addition to these data, costs also were estimated for the single adsorption process in which chromium would be disposed of in combination with spent carbon. For this estimate, the use of Nuchar carbon ($0.25/lb) was selected because it is significantly cheaper and showed loading capacities almost equivalent to Pittsburgh OL carbon (see Figure 11). On the basis of the 20 percent loading capacity that was demonstrated in the laboratory work, the raw material cost for this treatment would be $1.25 per pound of chromium, solely for make-up carbon. If partial recovery of carbon or chromium could be realized from the spent material, this cost would be reduced considerably.

In general, the cost data indicated that chemical costs for the carbon adsorption process range from $0.50 to $1.25 per pound of chromium removed, depending on whether or not the carbon is regenerated or disposed of after a single adsorption. The lower cost can be achieved with caustic regeneration, recovery of sodium chromate, and reuse of the sodium chromate within the plating plant for other operations such as conversion coatings. The possibility also exists for regeneration

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TABLE 29. COMPARISON OF CHEMICAL COSTS FOR ACTIVATED CARBON ADSORPTION AND CONVENTIONAL TREATMENT

	Amount of Reagent Used, lb/lb Cr	Cost, $/lb Cr
Carbon Adsorption and Acid Regeneration:		
20 Cycle Operation		
H_2SO_4 @ 3¢/lb	3.1	0.09
NaOH @ 6.5¢/lb	2.8	0.18
Carbon @ 40¢/lb	1.6	0.64
		0.91
50 Cycle Operation		
H_2SO_4 @ 3¢/lb	4.2	0.13
NaOH @ 6.5¢/lb	3.4	0.22
Carbon @ 40¢/lb	0.95	0.38
		0.73
Carbon Adsorption and Caustic Regeneration:		
20 Cycle Operation		
NaOH @ 6.5¢/lb	3.0	0.20
H_2SO_4 @ 3¢/lb	3.0	0.09
Carbon @ 40¢/lb	1.0	0.40
		0.69
50 Cycle Operation		
NaOH @ 6.5¢/lb	3.4	0.22
H_2SO_4 @ 3¢/lb	3.4	0.10
Carbon @ 40¢/lb	0.45	0.18
		0.50
Conventional Treatment With Sodium Bisulfite:		
$Na_2S_2O_5$ @ 11.5¢/lb	3.0	0.34
H_2SO_4 @ 3¢/lb	1.5	0.05
NaOH @ 6.5¢/lb	2.5	0.16
		0.55

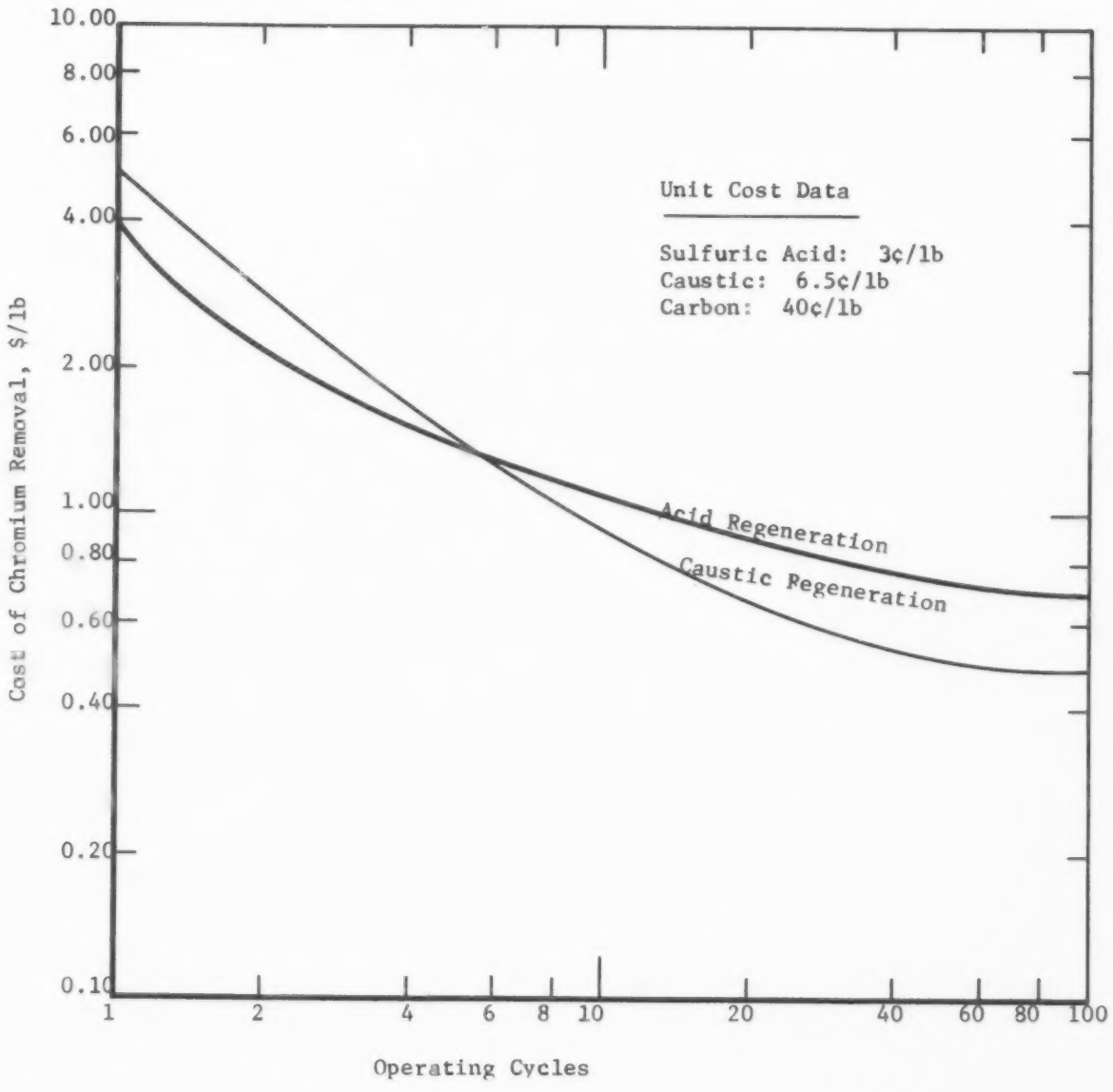

FIGURE 21. EFFECT OF OPERATING CYCLES ON CHEMICAL COSTS FOR TWO REGENERATION METHODS

of chromic acid by ion exchange methods. Whether or not recovery is feasible must be determined in each specific plating plant. Because of the higher cost of the acid regeneration method, which does not include costs for disposal of sludge, this method is considered the least practical of those studied during the program.

An economic comparison of the carbon process with conventional treatment also was made including other operating costs besides chemicals such as labor, amortization, etc. This comparison is shown in Table 30. The data indicate that operating costs for the carbon process are $5.37 per day based on the particular waste stream under consideration. Costs for conventional treatment are $7.34 per day.

TABLE 30. ESSENTIAL PLANT AND OPERATING COSTS FOR CARBON ADSORPTION AND CONVENTIONAL TREATMENT PROCESSES

	Carbon Process	Conventional Treatment
Essential Plant Cost; dollars[(a)]	5,500	8,000
Operating Costs; dollars/day		
(1) Chemicals[(a)]	3.00	3.30
(2) Labor @ $2.00/man-hr	1.00	2.00
(3) Supplies and Maintenance @ 0.003 percent of Plant Cost	0.17	0.24
(4) Amortization @ 0.0224 percent of Plant Cost	1.20	1.80
Totals	5.37	7.34

(a) Based on 8-hour day, waste flow rate of 15 gallons per minute, and contaminant level of 100 ppm, assuming unit cost data shown in Table 29.

SECTION VII

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APPENDIX

Conventional Methods for Treatment of Chromium Wastes

Methods used for Control Analyses

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SECTION IX

APPENDIX

Conventional Methods for Treatment of Chromium Wastes

The treatment of rinse waters from chromium plating operations usually consists of one or a combination of the following procedures:

(1) Reduction of hexavalent chromium to the trivalent form followed by the precipitation of the reduced chromium as the hydroxide

(2) Reclamation of chromic acid from the more concentrated rinse stream by evaporative or ion exchange techniques

(3) Removal of hexavalent chromium by the addition of compounds which form insoluble salts, e.g., barium chromate.

Reduction of Hexavalent Chromium and Precipitation of Chromic Hydroxide

Methods for reduction of hexavalent chromium vary with each particular plant. Common reducing agents are gaseous sulfur dioxide; sodium bisulfite, metabisulfite, or hydrosulfite; and ferrous sulfate.

Reduction with SO_2 is the method most commonly employed by many large plating plants. Basic equipment for this method consists of sulfonators for combining sulfur dioxide with water and agitated tanks for conducting the reduction. During reduction sulfuric acid is normally added to maintain an acid solution with a pH range of 2.0-3.0. Under these conditions, the reactions which occur are:

$$SO_2 + H_2O \rightarrow H_2SO_3$$

Sulfur dioxide — Water — Sulfurous acid

$$2CrO_3 + 3H_2SO_3 \rightarrow Cr_2(SO_4)_3 + 3H_2O$$

Chromic acid — Sulfurous acid — Chromic sulfate

The approximate chemical usage is 1 pound of SO_2 per pound of chromic acid (CrO_3) in the waste solution.

Other reducing agents, such as bisulfites or ferrous sulfate, also are used by plating plants for treatment of chromium wastewaters. Bisulfite may be added as a solid or as a solution. As with sulfur dioxide, the addition of sulfuric acid is required to maintain a pH of about 2 to 3

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to obtain rapid and complete reaction. The anhydrous form of sodium bisulfite ($Na_2S_2O_5$) or sodium metabisulfite also may be used. With ferrous sulfate larger quantities of sludge are produced than with sulfur dioxide or bisulfites. Some economic advantage for reduction with ferrous sulfate may be realized, however, if quantities of waste pickle liquor are readily available at the plating plant.

After reduction it may be possible to dispose directly of the effluent. The effluent may, however, require neutralization and precipitation of the now trivalent chromium (and other metals) before disposal to reduce its corrosiveness and whatever toxicity it may possess from such metals as nickel, copper, etc. If the precipitated solids after neutralization are too high or too potentially toxic to meet local regulations, the neutralized effluent may have to be given some sort of solids-liquid separation, such as sedimentation or filtration, prior to disposal.

Reclamation of Chromic Acid

In addition to the chemical operations discussed in the foregoing section, there are two commonly used physical methods that have been used in the treatment of rinse waters. These are ion exchange and evaporation.

Ion exchange has been widely used in the treatment of chromium and mixed rinse waters, not only for detoxification, but also for the recovery of chromium, water, and, in the case of hot rinses, of heat. Ion exchange processes may be particularly attractive as a means for detoxifying chromium rinse waters. Very little attention is required, except when regeneration of the exchange resins is necessary.

Regeneration, which amounts to removing the load of metals that the resins have absorbed, must be done periodically. This is accomplished by passing sulfuric acid through the resins to redissolve the metals. The regenerated solutions are greatly concentrated, but they are still toxic. If they are to be discharged to waste, then they require the chemical treatments previously discussed, but because they are concentrated and relatively low in volume compared to the original rinse waters, treatment can be carried out batchwise in small tanks. Recovery of chromium and other metals from the regenerating solutions also is a possibility; however, its economic feasibility for the smaller plater would require study. Water recovery for reuse in rinsing is a built-in feature of the ion exchange process.

Evaporative processes also have found some use for recovery of chromium from rinse waters. Generally, evaporative processes are economical only on concentrated rinses, such as those produced in still tanks or multi-stage countercurrent rinsing. If the smaller plater employs such rinsing techniques, evaporation processes may be worth consideration not only for the recovery of plating chemicals but also of rinse water.

Precipitation of Hexavalent Chromium

Removal of toxic chromium from wastewaters also can be effected by precipitation as hexavalent chromium. This method of treatment usually involves the use of barium salts to effect the formation of insoluble barium chromate. With barium chloride, for example, the following reaction takes place:

$BaCl_2$	+	Na_2CrO_4	→	$BaCrO_4$	+	$2NaCl$
Barium chloride		Sodium chromate		Insoluble barium chromate		Sodium chloride

The major disadvantage of this method is that the additions of barium chloride must be strictly controlled, as this chemical is highly toxic. The sludges produced also are toxic and may result in an additional disposal problem.

The process involving the precipitation of highly insoluble barium chromate generally will require a solids-liquid separation step before the effluent is disposed. Relatively few plants employ this process.

Methods used for Control Analyses

Simplified Test for Hexavalent Chromium

(1) Transfer a 50-ml sample, containing no more than 1.25 ppm of hexavalent chromium (predilute if necessary) to a 100-ml Erlenmeyer flask.

(2) Add 0.1 gram of solid reagent mixture made by grinding together 0.25 gram of 1,5 diphenylcarbohydrazide and 9.75 grams of tartaric acid.

(3) Shake vigorously until all the reagent is dissolved.

(4) Let stand 5 minutes to develop full color and measure the absorbance in a spectrophotometer at 540 mμ wavelength.

(5) Determine the hexavalent chromium concentration of the solution by comparison with a standard calibration curve (see Figure A-1).

(6) The color also may be compared against a set of permanent standards prepared in steps of 0.5 ppm by mixing together various proportions of crystal violet and safrinin.

Titrametric Method for Total Chromium

A control procedure for total chromium also was developed. This method involved the oxidation of chromium by ammonium persulfate in the presence of silver nitrate and titration of the chromium by the conventional ferrous sulfate-permanganate titration.

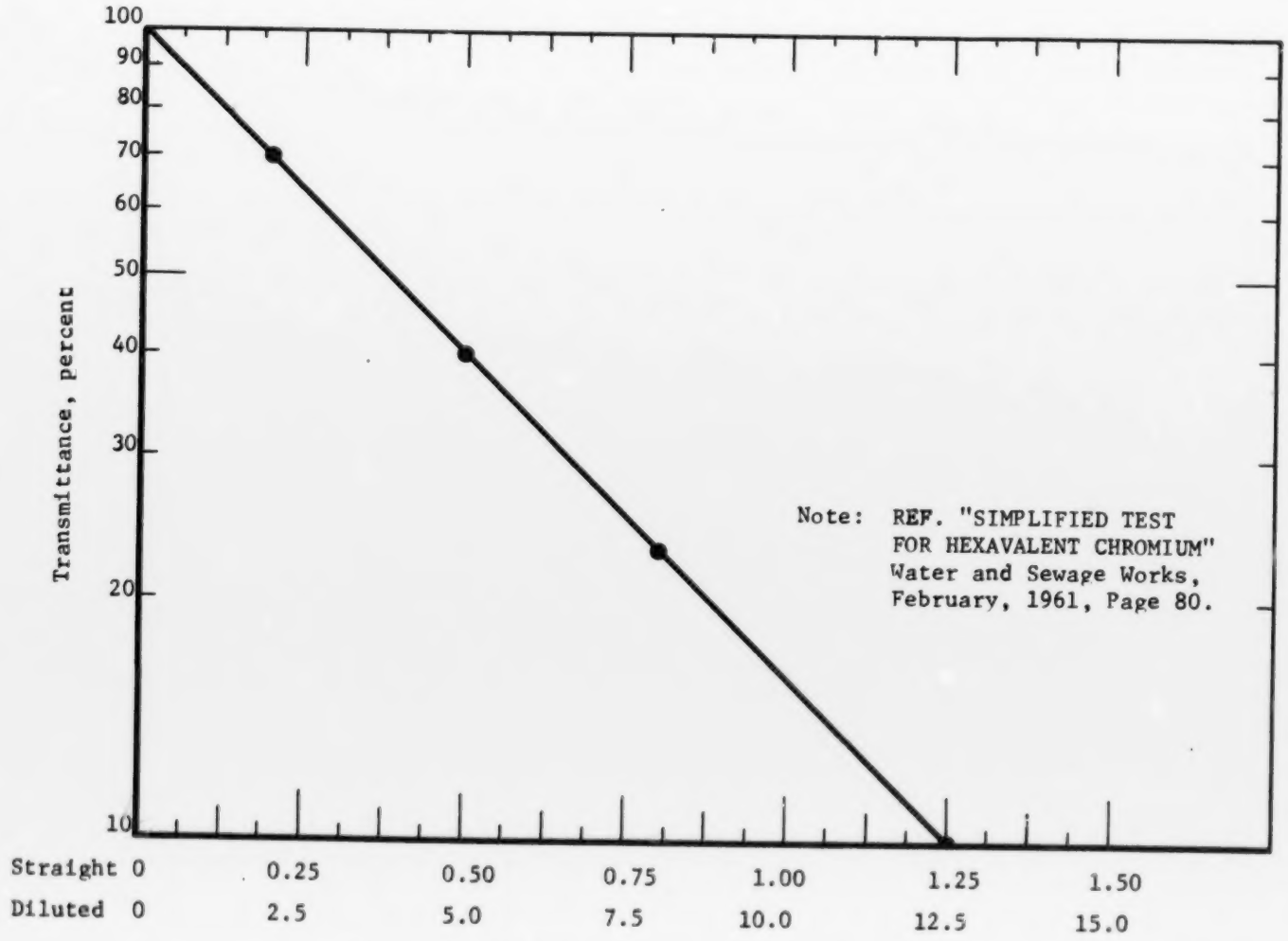

FIGURE 22. STANDARD CHROMIUM CURVE